

1 Introduction

Chemistry is primarily concerned not with the properties of single molecules but with periodic trends, homologous series and the like. It is, therefore, important that any method which we apply to the problem of molecular electronic structure depends linearly on the number of electrons in the system being studied. Meaningful comparisons of atoms and molecules of different sizes are then possible. This property has been termed size-consistency^{1,2}. Independent electron models, such as the widely used Hartree–Fock approximation, provide a size-consistent theory of atomic and molecular structure.

Independent-electron models account for the major proportion, typically 99.5%, of the non-relativistic electronic energy of an atom or molecule. The Hartree–Fock model describes not only the Fermi interactions of the electrons but also their averaged electrostatic interactions. It is unfortunate that the remaining energy is of the same order of magnitude as most energies of chemical interest. This remaining energy, the correlation energy, arises from the ‘instantaneous correlations’ of the individual electronic motions. Chemistry is primarily concerned with small energy differences, such as those between different nuclear geometries or different electronic states, and these differences may be seriously affected by the correlation energy.

In the past twenty years, there has been increasing interest in the calculation of correlation energies and other properties of atomic and molecular systems by means of diagrammatic many-body perturbation theory techniques^{3–9} due to Brueckner¹⁰ and Goldstone.¹¹ Diagrammatic many-body perturbation theory provides a simple pictorial representation of electron correlation effects in atoms

¹ J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem.*, 1976, **10**, 1.

² E. R. Davidson and D. W. Silver, *Chem. Phys. Lett.*, 1977, **52**, 403.

³ N. H. March, W. H. Young, and S. Sampanthar, ‘The Many-body Problem in Quantum Mechanics’, Cambridge University Press, 1967.

⁴ A. L. Fetter and J. D. Walecka, ‘Quantum Theory of Many-particle Systems’, McGraw-Hill, New York, 1971.

⁵ H. P. Kelly, *Adv. Chem. Phys.*, 1969, **14**, 129.

⁶ J. Paldus and J. Cizek, *Adv. Quantum Chem.*, 1975, **9**, 105.

⁷ I. Hubač and P. Čársky, *Top. Curr. Chem.*, 1978, **75**, 97.

⁸ S. Wilson, in ‘Proceedings of Daresbury Study Weekend’, Dec. 1977, ed. V. R. Saunders, Science Research Council, London, 1978.

⁹ S. Wilson, in ‘Proceedings of Daresbury Study Weekend’, November 1979, ed. M. F. Guest and S. Wilson, Science Research Council, London, 1980.

¹⁰ K. A. Brueckner, *Phys. Rev.*, 1955, **100**, 36.

¹¹ J. Goldstone, *Proc. R. Soc. London, Ser. A*, 1957, **239**, 267.

and molecules and also forms the basis of a tractable, non-iterative scheme for accurate calculations.^{5, 12-14} Perturbation theory provides perhaps the most systematic technique for the evaluation of corrections to independent electron models.

The many-body perturbation theory is so called because it can be applied to arbitrarily large systems. In fact, the theory was originally devised to treat infinite fermion systems. It leads to expressions for correlation corrections to independent electron models which have a linear dependence on the number of electrons being considered. If the theory is applied to a system A, giving an energy $E(A)$, and to a system B, giving an energy $E(B)$, and then to the combined system AB, where A and B are an infinite distance apart, then the energy of the super-system, $E(AB)$, is given by

$$E(AB) = E(A) + E(B) \quad (1)$$

The energy of any system may be written as a sum of the energies of its component parts *no matter how these components are defined*. This property is not shared by some of the other methods currently employed in the study of electron correlation, for example the widely used method of configuration mixing limited to single- and double-excitations, which, when a single determinantal reference function is used, leads to an expression for the correlation energy depending on the square root of the number of electrons under consideration.^{15, 16} Limited configuration mixing is not a size-consistent technique.

The diagrammatic many-body perturbation theory may be derived from the Rayleigh-Schrödinger perturbation expansion. Brueckner¹⁰ showed that certain terms arise in the Rayleigh-Schrödinger expansion which have a non-linear dependence on the number of electrons being studied. He showed that these unphysical terms cancel in each of the first few orders of the Rayleigh-Schrödinger perturbation series. Goldstone¹¹ generalized this result to all orders using the diagrammatic techniques of time-dependent perturbation theory. This leads to the linked diagram perturbation expansion.³⁻⁷ All terms corresponding to unlinked diagrams depend non-linearly on the number of electrons and thus mutually cancel in each order. This cancellation of unlinked diagrams not only eliminates unphysical terms but also leads to important computational simplifications.¹²⁻¹⁴

The pioneering work on the application of the many-body perturbation theory to atomic and molecular systems was performed by Kelly.^{5, 17-21} He applied the method to atoms using numerical solutions of the Hartree-Fock equations. Many other calculations on atomic systems were subsequently

¹² D. M. Silver, *Comput. Phys. Commun.*, 1978, **14**, 71.

¹³ D. M. Silver, *Comput. Phys. Commun.*, 1978, **14**, 81.

¹⁴ S. Wilson, *Comput. Phys. Commun.*, 1978, **14**, 91.

¹⁵ A. Meunier, B. Levy, and G. Berthier, *Int. J. Quantum Chem.*, 1976, **10**, 1061.

¹⁶ W. Kutzelnigg, A. Meunier, B. Levy, and G. Berthier, *Int. J. Quantum Chem.*, 1977, **12**, 77.

¹⁷ H. P. Kelly, *Phys. Rev.*, 1963, **131**, 684.

¹⁸ H. P. Kelly, *Phys. Rev.*, 1964, **136**, 896.

¹⁹ H. P. Kelly, *Phys. Rev.*, 1966, **144**, 39.

²⁰ H. P. Kelly, *Adv. Theor. Phys.*, 1968, **2**, 75.

²¹ H. P. Kelly, *Int. J. Quantum Chem. Symp.*, 1970, **3**, 349.

reported (e.g. refs. 22–26). The first molecular calculations using many-body perturbation theory used single-centre expansions and were limited to simple hydrides where it is possible to treat the hydrogen atoms as additional perturbations.^{27–31} More recently, the theory has been applied to arbitrary molecules by employing the algebraic approximation^{32–42} which is fundamental to most molecular calculations. In this approximation, single-particle state functions are parameterized in terms of a finite basis set. This is equivalent to replacing the true hamiltonian by a model hamiltonian whose domain is restricted to some subspace of the Hilbert space associated with the true hamiltonian.

In this article, the results of atomic calculations will only be considered when they are relevant to the molecular situation. This is the case in a number of areas where the application to atoms is well established but remains to be extended to molecules. This article is concerned with the application of the many-body perturbation theory to arbitrary molecular systems. Recent work^{43–44} has shown that this technique can be at least as if not more accurate than other techniques currently employed in the study of molecular electronic structure. The method is probably computationally more efficient than other schemes and certainly has a number of theoretical properties which make its use attractive. For example, in discussing the widely used method of configuration mixing, Shavitt states:⁴⁵ 'The fact that in a configuration interaction expansion unlinked cluster contributions can only be accounted for by including quadruple- (and higher-order) excitations is one of the principal drawbacks of the method. In contrast, such contributions are automatically accounted for without explicitly computing higher-order terms, in some cluster-based methods and in many-body perturbation theory. In this sense the CI expansion is much less compact and less efficient than these approaches and becomes progressively less efficient as the number of electrons increases.'

²² E. S. Chang, R. T. Pu, and T. P. Das, *Phys. Rev.*, 1968, **174**, 1.

²³ N. C. Dutta, C. Matsubara, R. T. Pu, and T. P. Das, *Phys. Rev.*, 1969, **177**, 33.

²⁴ R. T. Pu and E. S. Chang, *Phys. Rev.*, 1966, **151**, 31.

²⁵ T. Lee, N. C. Dutta, and T. P. Das, *Phys. Rev. A.*, 1970, **1**, 995.

²⁶ T. Lee, N. C. Dutta, and T. P. Das, *Phys. Rev. A.*, 1971, **4**, 1410.

²⁷ H. P. Kelly, *Phys. Rev. Lett.*, 1969, **23**, 455.

²⁸ J. H. Miller and H. P. Kelly, *Phys. Rev. Lett.*, 1971, **26**, 679.

²⁹ T. Lee, N. C. Dutta, and T. P. Das, *Phys. Rev. Lett.*, 1970, **25**, 204.

³⁰ T. Lee and T. P. Das, *Phys. Rev. A.*, 1972, **6**, 968.

³¹ C. M. Dutta, N. C. Dutta, and T. P. Das, *Phys. Rev. Lett.*, 1970, **25**, 1695.

³² S. Wilson and D. M. Silver, *Phys. Rev. A.*, 1976, **14**, 1949.

³³ J. M. Schulman and D. N. Kaufman, *J. Chem. Phys.*, 1970, **53**, 477.

³⁴ J. M. Schulman and D. N. Kaufman, *J. Chem. Phys.*, 1972, **57**, 2328.

³⁵ U. Kaldor, *J. Chem. Phys.*, 1975, **62**, 4634.

³⁶ U. Kaldor, *J. Chem. Phys.*, 1975, **63**, 2199.

³⁷ M. A. Robb, *Chem. Phys. Lett.*, 1973, **20**, 274; and in 'Computational Techniques in Quantum Chemistry and Molecular Physics', ed. G. H. F. Diercksen, B. T. Sutcliffe, and A. Veillard, D. Reidel, 1974, p. 435.

³⁸ U. Kaldor, *Phys. Rev. A.*, 1973, **7**, 427.

³⁹ R. J. Bartlett and D. M. Silver, *J. Chem. Phys.*, 1975, **62**, 3258; erratum, 1976, **64**, 4578.

⁴⁰ D. F. Freeman and M. Karplus, *J. Chem. Phys.*, 1976, **64**, 2641.

⁴¹ M. Urban, V. Kellö, and I. Hubač, *Chem. Phys. Lett.*, 1977, **51**, 170.

⁴² S. Prime and M. A. Robb, *Theor. Chim. Acta*, 1976, **42**, 181.

⁴³ S. Wilson and D. M. Silver, *J. Chem. Phys.*, 1977, **66**, 5400.

⁴⁴ S. Wilson and D. M. Silver, *J. Chem. Phys.*, 1977, **67**, 1649.

⁴⁵ I. Shavitt, in 'Modern Theoretical Chemistry', Vol 3, 'Methods of Electronic Structure Theory', ed. H. F. Schaefer III, Plenum Press, New York, 1977.

This article is divided into seven parts. The many-body perturbation theory is discussed in the next section. The algebraic approximation is discussed in some detail in section 3 since this approximation is fundamental to most molecular applications. In the fourth section, the truncation of the many-body perturbation series is discussed, and, since other approaches to the many-electron correlation problem may be regarded as different ways of truncating the many-body perturbation expansion, we briefly discuss the relation to other approaches. Computational aspects of many-body perturbative calculations are considered in section 5. In section 6, some typical applications to molecules are given. In the final section, some other aspects of the many-body perturbation theory of molecules are briefly discussed and possible directions for future investigations are outlined.

2 The Many-body Perturbation Theory

General Remarks.—In this section a brief introduction to the many-body perturbation theory is given. In the second part the partitioning technique due to Löwdin⁴⁶ and Feshbach⁴⁷ is used to give a straightforward and general introduction to perturbation expansions. The perturbation series of Lennard-Jones,⁴⁸ Brillouin,⁴⁹ and Wigner⁵⁰ is then described. This series is not suitable for application to many-particle systems and we, therefore, indicate how the many-body perturbation theory can be derived from the Rayleigh-Schrödinger perturbation theory. Diagrammatic rules and conventions are then introduced enabling the diagrammatic formulation of the many-body perturbation theory to be given. Some generalizations of the theory are briefly considered in the final part of this section.

The Partitioning Technique.—Let P denote the projector onto some zero-order model wave function $|\Phi_0\rangle$ and Q its complement. The electronic Schrödinger equation

$$\mathcal{H}|\Psi\rangle = \mathcal{E}|\Psi\rangle \quad (2)$$

may then be written as a two by two block matrix equation

$$\begin{pmatrix} P\mathcal{H}P & P\mathcal{H}Q \\ Q\mathcal{H}P & Q\mathcal{H}Q \end{pmatrix} \begin{pmatrix} P\Psi \\ Q\Psi \end{pmatrix} = \mathcal{E} \begin{pmatrix} P\Psi \\ Q\Psi \end{pmatrix} \quad (3)$$

where $|\Phi_0\rangle = P|\Psi_0\rangle \cdot Q|\Psi_0\rangle$ can now be eliminated to produce the effective Schrödinger equation

$$[P\mathcal{H}P + P\mathcal{H}Q(\mathcal{E}_0 - Q\mathcal{H}Q)^{-1}Q\mathcal{H}P]|\Phi_0\rangle = \mathcal{E}_0|\Phi_0\rangle \quad (4)$$

or

$$\mathcal{H}_{\text{eff}}|\Phi_0\rangle = \mathcal{E}_0|\Phi_0\rangle \quad (5)$$

where

$$\mathcal{H}_{\text{eff}} = [P\mathcal{H}P + P\mathcal{H}Q(\mathcal{E}_0 - Q\mathcal{H}Q)^{-1}Q\mathcal{H}P] \quad (6)$$

⁴⁶ P. O. Löwdin, *J. Math. Phys.*, 1962, 3, 969 and references therein.

⁴⁷ H. Feshbach, *Ann. Phys. (N.Y.)*, 1962, 19, 287.

⁴⁸ J. E. Lennard-Jones, *Proc. R. Soc. London, Ser. A.*, 1930, 129, 598.

⁴⁹ L. Brillouin, *J. Physique*, 1932, 7, 373.

⁵⁰ E. P. Wigner, *Math. u. naturw. Anz. ungar. Akad. Wiss.*, 1935, 53, 475.

This effective hamiltonian has eigenfunctions in the model space but has the exact energy as an eigenvalue.

Various forms of perturbation theory result from different expansions of the inverse in the effective hamiltonian using the identity

$$(\hat{A} - \hat{B})^{-1} = \sum_{n=0}^{n=\infty} \hat{A}^{-1} (\hat{B} \hat{A}^{-1})^n \quad (7)$$

If \mathcal{H}_0 denotes some zero-order hamiltonian and E_0 its ground state eigenvalue then the perturbation series of Lennard-Jones,⁴⁸ Brillouin,⁴⁹ and Wigner⁵⁰ is obtained by putting

$$\hat{A} = \mathcal{E}_0 - \mathcal{H}_0 \quad (8)$$

and

$$\hat{B} = \mathcal{H} - \mathcal{H}_0 \quad (9)$$

The Rayleigh-Schrödinger perturbation expansion is obtained by putting

$$\hat{A} = \hat{E}_0 - \mathcal{H}_0 \quad (10)$$

and

$$\hat{B} = \mathcal{H} - \mathcal{H}_0 - \mathcal{E} + E_0 \quad (11)$$

Lennard-Jones Brillouin Wigner Perturbation Theory.—Let us write the total hamiltonian operator as a sum of a zero-order operator and a perturbation

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \quad (12)$$

with

$$\mathcal{H}_0 |\Phi_i\rangle = E_i |\Phi_i\rangle \quad (13)$$

and

$$\mathcal{H} |\Psi_i\rangle = \mathcal{E}_i |\Psi_i\rangle = (E_i + \Delta E_i) |\Psi_i\rangle \quad (14)$$

We introduce the projection operators

$$P_0 = |\Phi_0\rangle\langle\Phi_0| \quad (15)$$

and

$$Q_0 = I - P_0 \quad (16)$$

and employ the intermediate normalization convention

$$\langle\Phi_0|\Psi_0\rangle = 1 = \langle\Phi_0|\Phi_0\rangle \quad (17)$$

Now we can define the wave operator, $\hat{\Omega}$, with the following properties

$$|\Psi_0\rangle = \hat{\Omega} |\Phi_0\rangle \quad (18)$$

and

$$P_0 \hat{\Omega} = P_0 \quad (19)$$

$$\hat{\Omega} P_0 = \hat{\Omega} \quad (20)$$

$$\hat{\Omega} Q_0 = 0 \quad (21)$$

and thus obtain an expression for the level shift, ΔE_0 , for the ground state

$$\begin{aligned}\Delta E_0 &= \sum_{i=1}^{i=\infty} E_0^{(i)} \\ &= \langle \Phi_0 | \mathcal{H}_1 | \Psi_0 \rangle \\ &= \langle \Phi_0 | \mathcal{H}_1 \Omega | \Phi_0 \rangle \\ &= \langle \Phi_0 | \hat{\mathcal{V}} | \Phi_0 \rangle\end{aligned}\quad (22)$$

where the reaction operator, $\hat{\mathcal{V}}$, is given by

$$\hat{\mathcal{V}} = \mathcal{H}_1 \Omega \quad (23)$$

In Lennard-Jones Brillouin Wigner perturbation theory the wave operator is written as

$$\Omega = \left[I + \sum_{n=1}^{n=\infty} \left(\frac{Q_0}{E_0 + \Delta E_0 - \mathcal{H}_0} \mathcal{H}_1 \right)^n \right] P_0 \quad (24)$$

and the level shift has the form

$$\Delta E_0 = \langle \Phi_0 | \mathcal{H}_1 \left[I + \sum_{n=1}^{n=\infty} \left(\frac{Q_0}{E_0 + \Delta E_0 - \mathcal{H}_0} \mathcal{H}_1 \right)^n \right] | \Phi_0 \rangle \quad (25)$$

These expressions for the wave operator and the reaction operator are formally equivalent to the integral equations

$$\Omega = P_0 + \frac{Q_0}{E_0 + \Delta E_0 - \mathcal{H}_0} \mathcal{H}_1 \Omega \quad (26)$$

and

$$\hat{\mathcal{V}} = \mathcal{H}_1 P_0 + \mathcal{H}_1 \frac{Q_0}{E_0 + \Delta E_0 - \mathcal{H}_0} \hat{\mathcal{V}} \quad (27)$$

from which the corresponding perturbation expansions can be obtained by iteration.

Explicitly, the first few terms in the Lennard-Jones Brillouin Wigner perturbation series take the form

$$E_0 = \langle \Phi_0 | \mathcal{H}_0 | \Phi_0 \rangle \quad (28a)$$

$$E_0^{(1)} = \langle \Phi_0 | \mathcal{H}_1 | \Phi_0 \rangle \quad (28b)$$

$$E_0^{(2)} = \langle \Phi_0 | \mathcal{H}_1 \mathcal{R} \mathcal{H}_1 | \Phi_0 \rangle \quad (28c)$$

$$E_0^{(3)} = \langle \Phi_0 | \mathcal{H}_1 (\mathcal{R} \mathcal{H}_1)^2 | \Phi_0 \rangle \quad (28d)$$

$$E_0^{(4)} = \langle \Phi_0 | \mathcal{H}_1 (\mathcal{R} \mathcal{H}_1)^3 | \Phi_0 \rangle \quad (28e)$$

$$E_0^{(5)} = \langle \Phi_0 | \mathcal{H}_1 (\mathcal{R} \mathcal{H}_1)^4 | \Phi_0 \rangle \quad (28f)$$

...

where \mathcal{R} is the resolvent

$$\mathcal{R} = \frac{Q_0}{\mathcal{E} - \mathcal{H}_0} \quad (29)$$

The Lennard-Jones Brillouin Wigner perturbation expansion is a simple geometric series. However, it contains the unknown exact energy within the denominators. This expansion is, therefore, not a simple power series in the perturbation.

The perturbation theory of Lennard-Jones, Brillouin, and Wigner is not size consistent.

Rayleigh-Schrödinger Perturbation Theory.—In Rayleigh-Schrödinger perturbation theory the unknown energy in the denominators of the Lennard-Jones Brillouin Wigner expansion is avoided. This enables a size-consistent theory to be derived.

The wave operator, $\hat{\Omega}$, may be written in an alternative form by replacing \mathcal{H}_0 by $\mathcal{H}_0 + Q_0 \Delta E_0 Q_0$ and \mathcal{H}_1 by $\mathcal{H}_1 - Q_0 \Delta E_0 Q_0$ giving

$$\hat{\Omega} = P_0 + \frac{Q_0}{E_0 - \mathcal{H}_0} (\mathcal{H}_1 - \Delta E_0) \hat{\Omega} \quad (30)$$

Rearranging this expression in terms of powers of the perturbation, \mathcal{H}_1 , we obtain

$$\hat{\Omega}^{(n)} = \frac{Q_0}{E_0 - \mathcal{H}_0} \left[\mathcal{H}_1 \hat{\Omega}^{(n-1)} - \sum_{j=1}^{n-1} E_0^{(j)} \hat{\Omega}^{(n-j)} \right] \quad (31)$$

The j -th order energy is given by

$$E_0^{(j)} = \langle \Phi_0 | \mathcal{H}_1 \hat{\Omega}^{(n-1)} | \Phi_0 \rangle \quad (32)$$

Explicitly, the first few terms in the Rayleigh-Schrödinger perturbation expansion may be written in the form:

$$E_0 = \langle \Phi_0 | \mathcal{H}_0 | \Phi_0 \rangle \quad (33a)$$

$$E_0^{(1)} = \langle \Phi_0 | \mathcal{H}_1 | \Phi_0 \rangle \quad (33b)$$

$$E_0^{(2)} = \langle \Phi_0 | \mathcal{H}_1 \hat{\mathcal{R}}_0 \mathcal{H}_1 | \Phi_0 \rangle \quad (33c)$$

$$E_0^{(3)} = \langle \Phi_0 | \mathcal{H}_1 (\hat{\mathcal{R}}_0 \mathcal{H}_1)^2 | \Phi_0 \rangle - E_0^{(1)} \langle \Phi_0 | \mathcal{H}_1 \hat{\mathcal{R}}_0^2 \mathcal{H}_1 | \Phi_0 \rangle \quad (33d)$$

$$E_0^{(4)} = \langle \Phi_0 | \mathcal{H}_1 (\hat{\mathcal{R}}_0 \mathcal{H}_1)^3 | \Phi_0 \rangle - E_0^{(1)} \{ \langle \Phi_0 | \mathcal{H}_1 \hat{\mathcal{R}}_0 \mathcal{H}_1 \hat{\mathcal{R}}_0^2 \mathcal{H}_1 | \Phi_0 \rangle + \langle \Phi_0 | \mathcal{H}_1 \hat{\mathcal{R}}_0^2 \mathcal{H}_1 \hat{\mathcal{R}}_0 \mathcal{H}_1 | \Phi_0 \rangle \} - E_0^{(2)} \langle \Phi_0 | \mathcal{H}_1 \hat{\mathcal{R}}_0 \mathcal{H}_1 | \Phi_0 \rangle \quad (33e)$$

...

where $\hat{\mathcal{R}}_0$ is the reduced resolvent

$$\hat{\mathcal{R}}_0 = \frac{Q_0}{E_0 - \mathcal{H}_0} \quad (34)$$

Clearly, the terms other than the first in the expressions for $E_0^{(3)}$, $E_0^{(4)}$, $E_0^{(5)}$, etc. depend on the number of electrons in a non-linear fashion. These terms exactly cancel components of the first terms in each of the expressions which also have a non-linear dependence on the number of electrons.

The Many-body Perturbation Theory.—The Rayleigh-Schrödinger form of perturbation theory provides an expansion for expectation values which have a linear dependence on the number of electrons in the system, N . In each order, other than zero-, first-, and second-order, terms arise which have a non-linear dependence on N . Brueckner¹⁰ showed that for the first few orders the terms having a non-linear dependence on N mutually cancel in each order. Goldstone¹¹ showed, using time-dependent perturbation theory, that this result can be generalized to all orders. The terms having a non-linear dependence on N may be associated with unlinked diagrams while those having the desired linear

dependence on N are associated with linked diagrams. This is the well known linked diagram theorem of many-body perturbation theory.

It should perhaps be stated at this point that the use of diagrams in the many-body perturbation theory is not obligatory. The whole of the theoretical apparatus can be set up in entirely algebraic terms. However, the diagrams are both more physical and easier to handle than the algebraic expressions and it is well worth the effort required to familiarize oneself with the diagrammatic rules and conventions.

The linked diagram expansion has, indeed, been derived by many authors and we shall, therefore, content ourselves with a brief outline of the Goldstone derivation here referring the interested reader elsewhere for full details.³⁻⁵

Before outlining the Goldstone treatment, we shall briefly mention some other derivations of the linked diagram theorem. Of particular interest is the derivation given by Brandow⁵¹ which is based on the expansion of the energy-dependent denominators in the Lennard-Jones Brillouin Wigner perturbation theory. Paldus and Cizek⁶ have given a time-independent derivation using a generalization of Wick's theorem⁵² for time-independent problems. This approach has also been followed by Hubac and Carsky.⁷

The many-body perturbation theory is developed in terms of some set of single particle states, ϕ_p , which are eigenfunctions of some single-particle operator, f ,

$$f\phi_p = \epsilon_p\phi_p \quad (35)$$

with eigenvalues ϵ_p . In the second-quantized formalism the zero-order hamiltonian has the form

$$\mathcal{H}_0 = \int d\mathbf{r}_1 \psi^\dagger(\mathbf{r}_1) f(\mathbf{r}_1) \psi(\mathbf{r}_1) \quad (36)$$

and the perturbation operator may be written as

$$\mathcal{H}_1 = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi^\dagger(\mathbf{r}_1) \psi^\dagger(\mathbf{r}_2) g(\mathbf{r}_1, \mathbf{r}_2) \psi(\mathbf{r}_2) \psi(\mathbf{r}_1) - \int d\mathbf{r}_1 \psi^\dagger(\mathbf{r}_1) V(\mathbf{r}_1) \psi(\mathbf{r}_1) \quad (37)$$

where $\psi^\dagger(\mathbf{r}_1)$ and $\psi(\mathbf{r}_1)$ are the usual creation and annihilation field operators, $g(\mathbf{r}_1, \mathbf{r}_2)$ is the two-electron potential, and $V(\mathbf{r}_1)$ is the effective potential which is added to the bare-nucleus hamiltonian to give the one-electron operator $f(\mathbf{r}_1)$. There is, of course, considerable freedom in the choice of the effective potential.

Use of the interaction representation in time-dependent perturbation theory and an adiabatic switching, ($|\alpha|t$), of the perturbation yields the evolution operator

$$\hat{U}^\alpha(t, -\infty) = \hat{I} + \sum_{n=1}^{n=\infty} \hat{U}_n^\alpha(t, -\infty) \quad (38)$$

where \hat{I} is the identity operator and $\hat{U}_n^\alpha(t, -\infty)$ is proportional to the n th power of the perturbation:

$$\hat{U}_n^\alpha(t, -\infty) = (-i)^n \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \dots \int_{-\infty}^{t_{n-1}} dt_n \mathcal{H}_1(t_1) \mathcal{H}_1(t_2) \dots \mathcal{H}_1(t_n) \quad (39)$$

⁵¹ B. H. Brandow, *Rev. Mod. Phys.*, 1967, **39**, 771.

⁵² G. C. Wick, *Phys. Rev.*, 1950, **80**, 268.

$$\mathcal{H}_1(t) = \exp(i\mathcal{H}_0 t) \mathcal{H}_1 \exp(-i\mathcal{H}_0 t) \quad (40)$$

The function

$$|\Psi_0\rangle = \left[\lim_{\alpha \rightarrow 0} \frac{\hat{U}^\alpha(t, -\infty) |\Phi_0\rangle}{\langle \Phi_0 | \hat{U}^\alpha(t, -\infty) | \Phi_0 \rangle} \right]_{t=0} \quad (41)$$

which obeys the intermediate normalization condition $\langle \Phi_0 | \Psi_0 \rangle = 1$ is a well-defined eigenfunction of the total hamiltonian.⁵³ The total energy is given by

$$E = E_0 + \Delta E_0 \quad (42)$$

where the level shift is

$$\Delta E_0 = \left[\lim_{\alpha \rightarrow 0} \frac{\langle \Phi_0 | \mathcal{H}_1(t) \hat{U}^\alpha(t, -\infty) | \Phi_0 \rangle}{\langle \Phi_0 | \hat{U}^\alpha(t, -\infty) | \Phi_0 \rangle} \right]_{t=0} \quad (43)$$

The denominator in this equation may be written as

$$\exp[\langle \Phi_0 | \hat{U}^\alpha(0, -\infty) | \Phi_0 \rangle]_L \quad (44)$$

where the subscript L indicates that only terms described by linked diagrams are to be included. From equations (41) and (44), we obtain after taking the limit, the Goldstone expression for the wave function

$$|\Psi_0\rangle = (\hat{U}(0, -\infty) | \Phi_0 \rangle)_L \quad (45)$$

and the level shift

$$\Delta E_0 = \langle \Phi_0 | \mathcal{H}_1(0) \hat{U}(0, -\infty) | \Phi_0 \rangle_L \quad (46)$$

Analysis of the products of field operators in these equations leads to a representation of the wave function and of the level shift in terms of diagrams of the type first introduced by Feynman. These diagrams provide a simple pictorial description of electron correlation effects in terms of the particle-hole formalism.

Diagrammatic Conventions.—A diagram is a device through which a corresponding algebraic expression can be obtained. A number of different diagrammatic conventions are in use. We shall follow the work of Brandow⁵¹ below and then discuss briefly its relation with other commonly used conventions.

The basic elements of the diagrams are shown in Figure 1. Figure 1 (a) shows the diagrammatic representation of a one-electron operator matrix element. Figure 1 (b) shows the representation of a two-electron matrix which in the Brandow scheme includes permutation of the two electrons involved. Upward (downward) directed lines represent particles (holes) created above (below) the Fermi level when an electron is excited.

The rules for performing the translation from a given diagram of the Brandow form to the corresponding algebraic expression are as follows:

- (i) Label each downward directed line with a unique 'hole' index: i, j, k, \dots and label each upward directed line with a unique 'particle' index a, b, c, \dots
- (ii) There is a summation over each unique hole and particle index covering all permissible values of these indices.

⁵³ M. Gell-mann and F. Low, *Phys. Rev.*, 1951, **84**, 350.

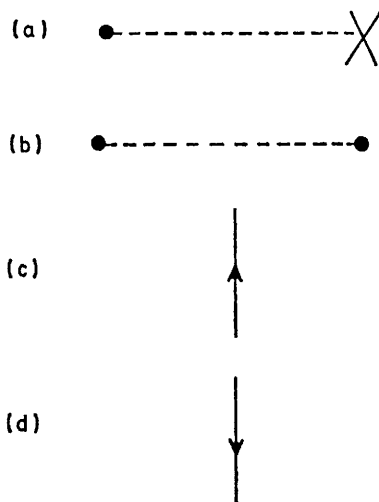


Figure 1 Diagram elements: (a) one-electron operator, (b) two-electron operator, (c) particle line, (d) hole line

(iii) The numerator of the summand consists of a product of antisymmetrized two-electron integrals

$$\mathcal{J}_{pqrs} = \int dr_1 \int dr_2 \phi_p^*(r_1) \phi_q^*(r_2) r_{12}^{-1} \{ \phi_r(r_1) \phi_s(r_2) - \phi_s(r_1) \phi_r(r_2) \} \quad (47)$$

where ϕ is a one-electron function and r_{12} is the inter-electronic separation. For each interaction, *i.e.* horizontal dashed line, there is an integral of this type. The orbital indices can be read from the labelled diagram. Hence the indices p, q, r, s , should correspond to hole or particle lines entering or leaving the interaction in the following order: 'left-out, right-out, left-in, right-in', respectively.

(iv) The denominator of the summand consists of a product of factors. There are $n-1$ factors corresponding to an n th order diagram such that there is a denominator factor arising between adjacent interactions in the diagram. A denominator factor consists of the terms

$$\sum_i \varepsilon_i - \sum_a \varepsilon_a \quad (48)$$

where the first summation is over all hole lines that extend between the adjacent interactions and the second summation is over all particle lines that extend between the interactions. The ε are the one-electron orbital energies.

(v) There is a multiplicative factor of $1/2$ for each pair of 'equivalent' lines. An equivalent pair of lines is defined to be two lines beginning at one interaction and ending at another and both going in the same direction.

(vi) There is a multiplicative factor of $(-1)^p$, where p is the sum of h and l . h is the number of unique hole lines in the diagram and l is the number of fermion loops. A fermion loop is determined by following the hole and particle lines in the direction of the arrows to form a continuous closed loop.

As an example of the application of these rules consider the diagram representing the third-order 'hole-hole' energy, E_3 (h-h), shown in Figure 2(a). The lines in this diagram may be labelled to give Figure 2(b). The lowest interaction line gives rise to the integral \mathcal{J}_{ijab} , the middle line implies the integral $\mathcal{J}_{kl ij}$, and the upper line the integral \mathcal{J}_{abkl} . The lower half of the diagram yields the denominator factor $\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b$, while the upper half corresponds to a denominator

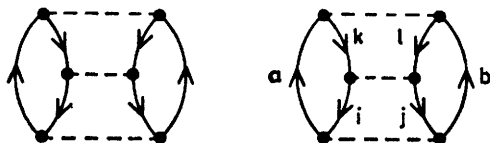


Figure 2 Diagrammatic representation of the third-order 'hole-particle' energy

factor of $\varepsilon_k + \varepsilon_l - \varepsilon_a - \varepsilon_b$. The lines labelled i and j , k and l , and a and b are equivalent pairs giving a factor of $(1/2)^3 = 1/8$. There are two fermion loops and four unique hole lines giving a factor of $(-1)^6 = 1$. E_3 (h-h) thus corresponds to the algebraic expression

$$\frac{1}{8} \sum_{ijkl} \sum_{ab} \frac{\mathcal{J}_{ijab} \mathcal{J}_{kl ij} \mathcal{J}_{abkl}}{\mathcal{D}_{ijab} \mathcal{D}_{klab}} \quad (49)$$

where

$$\mathcal{D}_{pq\ldots rs\ldots} = \varepsilon_p + \varepsilon_q + \ldots - \varepsilon_r - \varepsilon_s - \ldots \quad (50)$$

Two other diagrammatic conventions are commonly used in perturbation theory. The Goldstone diagrams¹¹ are similar to those of Brandow⁵¹ except that the interaction lines do not include permutation of the two electrons involved. Thus there is a set of Goldstone diagrams, which are related by electron exchange, corresponding to each Brandow diagram. The diagrams of Hugenholtz⁵⁴ are in one-to-one correspondence with those of Brandow. The Hugenholtz diagrams can be obtained from the Brandow diagrams by replacing the interaction lines in the latter by a single dot. This correspondence is illustrated in Figure 3.

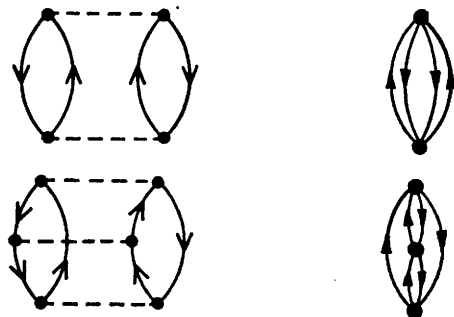


Figure 3 Correspondence between Brandow and Hugenholtz diagrams

⁵⁴ N. H. Hugenholtz, *Physica*, 1957, 23, 481.

Diagrammatic Perturbation Theory.—The zero-order and first-order terms in the diagrammatic perturbation theory for a closed-shell molecule, which is described by a single determinantal wave function in zero-order, sum to the expectation value of the total hamiltonian for that wave function. Thus for a Hartree-Fock reference function the sum of the zero-order and the first-order energies is the self-consistent-field energy. The correlation energy is given by the sum of the second-order and higher-order terms.

The second-order and third-order diagrams, using the Brandow antisymmetrized vertices convention, are displayed in Figure 4. When the Hartree-Fock reference function is employed, there is one second-order diagram and three third-order diagrams, which are distinguished by the type of central interaction line: the particle-particle (p-p) diagram, the hole-particle (h-p) diagram, and the hole-hole (h-h) diagram. The second-order and third-order (p-p) diagrams have only two hole lines; the correlation effects which they describe are, therefore, exclusively two-body. The third-order (h-p) diagram contains three hole lines and can therefore describe three-body interactions; however, if two of the hole lines are associated with the same single-particle state, then it describes two-body correlations. Finally, the third-order (h-h) diagram has four hole lines and can describe two-body, three-body, and four-body interactions.

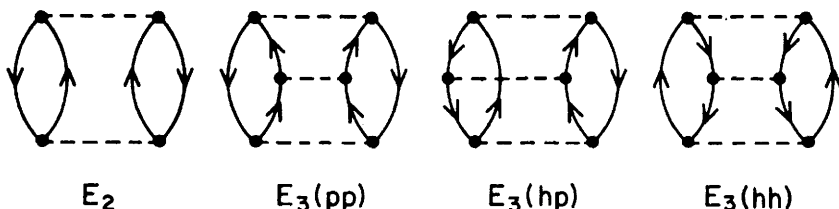


Figure 4 Second- and third-order diagrams which arise when the Hartree-Fock model is used to obtain a reference function

Explicit expressions corresponding to the four diagrams shown in Figure 4 can be written down by following the rules given in the previous section. The second-order energy expression has the form

$$E_2 = \frac{1}{4} \sum_{ij} \sum_{ab} \frac{\mathcal{J}_{ijab} \mathcal{J}_{abij}}{\mathcal{D}_{ijab} - d_{ijab}} \quad (51)$$

where the d_{ijab} will be discussed below but in the immediate discussion should be taken to be zero. The third-order (p-p) energy may be written

$$E_3(p-p) = \frac{1}{8} \sum_{ij} \sum_{abcd} \frac{\mathcal{J}_{ijab} \mathcal{J}_{abcd} \mathcal{J}_{cdij}}{(\mathcal{D}_{ijab} - d_{ijab})(\mathcal{D}_{ijcd} - d_{ijcd})} \quad (52)$$

the third-order (h-p) energy written as

$$E_3(h-p) = \sum_{ijk} \sum_{abc} \frac{\mathcal{J}_{ijab} \mathcal{J}_{akic} \mathcal{J}_{bcjk}}{(\mathcal{D}_{ijab} - d_{ijab})(\mathcal{D}_{jkbc} - d_{jkbc})} \quad (53)$$

and the third-order (h-h) energy written as

$$E_3(h-h) = \frac{1}{8} \sum_{ijkl} \sum_{ab} \frac{\mathcal{J}_{ijab} \mathcal{J}_{kl ij} \mathcal{J}_{abkl}}{(\mathcal{D}_{ijab} - d_{ijab})(\mathcal{D}_{klab} - d_{klab})} \quad (54)$$

Note that all of the above expressions are written in terms of single electron functions and no reference is made to many-electron functions. This is a fundamental characteristic of the many-body perturbation theoretic approach to the correlation problem.

In the above expressions the N -electron Hartree–Fock model hamiltonian, \mathcal{H}_0 , was used as a zero-order operator. This leads to the perturbation series of the type first discussed through second-order by Møller and Plesset.^{55, 56} However, it is clear that any operator \hat{X} obeying the relation

$$[\mathcal{H}_0, \hat{X}] = 0 \Rightarrow \hat{X} = \sum_{\kappa} |\kappa\rangle\langle\kappa| \hat{X} |\kappa\rangle\langle\kappa| \quad (55)$$

where $|\kappa\rangle$ is an eigenfunction of \mathcal{H}_0 , may be used to develop a perturbation series. The operator

$$\mathcal{H}_{\text{shifted}} = \sum_{\kappa} |\kappa\rangle\langle\kappa| \mathcal{H} |\kappa\rangle\langle\kappa| \quad (56)$$

gives rise to the shifted, or Epstein–Nesbet,^{57–59} perturbation series. The resulting perturbation expansion has the same diagrammatic representation as that discussed above for that based on the Hartree–Fock model hamiltonian. The corresponding algebraic expressions are as given above in equations (50)–(54) except that

(i) in third-order terms we omit the diagonal scattering terms, *i.e.* the summations are modified as follows

$$\sum_{ij} \sum_{abcd} \longrightarrow \sum_{ij} \sum_{\substack{abcd \\ ab \neq cd}} \quad (57a)$$

$$\sum_{ijk} \sum_{abc} \longrightarrow \sum_{\substack{ijk \\ i \neq k}} \sum_{\substack{abc \\ a \neq c}} \quad (57b)$$

$$\sum_{ijkl} \sum_{ab} \longrightarrow \sum_{\substack{ijkl \\ ij \neq kl}} \sum_{ab} \quad (57c)$$

(ii) the denominators are ‘shifted’ by

$$d_{ijab} = \mathcal{J}_{ijij} + \mathcal{J}_{abab} + \mathcal{J}_{iaai} + \mathcal{J}_{ibbi} + \mathcal{J}_{jaaj} + \mathcal{J}_{jbbj} \quad (58)$$

The use of shifted denominators may also be interpreted as the inclusion of certain higher-order terms in the perturbation series based on the Hartree–Fock model hamiltonian.

The sum of the perturbation expansion to infinite order is, of course, independent of the choice of the zero-order operator. Assuming that the perturbation series have converged, the model, or Møller–Plesset, and shifted, or Epstein–Nesbet, perturbation series will give identical results at sufficiently high order.

Generalizations.—The expansion of Brueckner¹⁰ and Goldstone¹¹ can only be applied when the unperturbed wave function can be described by a single Slater

⁵⁵ Chr. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.

⁵⁶ J. S. Binkley and J. A. Pople, *Int. J. Quantum Chem.*, 1975, **9**, 229.

⁵⁷ P. S. Epstein, *Phys. Rev.*, 1926, **28**, 695.

⁵⁸ R. K. Nesbet, *Proc. R. Soc. London, Ser. A*, 1955, **230**, 312, 322.

⁵⁹ P. Claverie, S. Diner, and J. Malrieu, *Int. J. Quantum Chem.*, 1967, **1**, 751.

determinant. Brandow^{51,60} has derived a quasi-degenerate many-body perturbation theory which has been applied by Kaldor and his co-workers^{61,62} to some open-shell systems which cannot be described by a single determinant in zero-order. The formulation is developed with respect to a multi-determinant reference function. In Brandow's formalism,^{51,60} the occupied orbitals are divided into 'core' orbitals, which are occupied in all of the determinants included in the reference function, and 'valence' orbitals, which are only occupied in some of the determinants in the reference function. The problem of applying the many-body perturbation theory to open-shell and multiconfiguration reference functions has been considered by a number of authors.^{51,60-74} Brandow's derivation^{51,60} is time-independent. The derivation of Kuo *et al.*⁷¹ is a generalization of the time-dependent treatment of Goldstone.¹¹ Johnson and Baranger⁷⁰ give a detailed discussion of the so-called folded diagrams which arise in the generalized expansion. The work of Lindgren,⁷² Levy,⁷³ and Kvasnicka⁷⁴ in this area should also be noted. The work of Hegarty and Robb⁷⁵ using quasi-degenerate Rayleigh-Schrödinger perturbation theory is also of interest. In almost all derivations of quasi-degenerate many-body perturbation theory given to date, it is assumed that the model space, the space spanned by the determinants in the reference function, is complete; that is, all possible occupations of the valence orbitals are included. However, this definition of the model space is likely to cause the appearance of intruder states. Intruder states are determinants which have to be included in the reference function in order to complete the model space but which have an energy significantly above that of other determinants in the reference function. The presence of intruder states can impair or even destroy the convergence of the perturbation expansion. A recent theoretical development in this area is the work of Hose and Kaldor⁷⁶ which allows an incomplete model space to be used and thus enables intruder states to be omitted from the reference function.

A second generalization of the many-body perturbation theory, which would certainly be useful in the calculation of potential energy curves and surfaces, would be to use a reference function constructed from non-orthogonal orbitals.

⁶⁰ B. H. Brandow, *Adv. Quantum Chem.*, 1977, **10**, 187.

⁶¹ U. Kaldor, *J. Chem. Phys.*, 1975, **62**, 4364; 1975, **63**, 2199.

⁶² P. S. Stern and U. Kaldor, *J. Chem. Phys.*, 1976, **64**, 2002.

⁶³ C. Bloch, *Nuclear Phys.*, 1958, **6**, 329.

⁶⁴ J. Des Cloizeaux, *Nuclear Phys.*, 1960, **20**, 321.

⁶⁵ H. Primas, *Helv. Phys. Acta*, 1961, **34**, 1961.

⁶⁶ H. Primas, *Rev. Mod. Phys.*, 1963, **35**, 710.

⁶⁷ T. Morita, *Progr. Theor. Phys.*, 1963, **29**, 351.

⁶⁸ H. P. Kelly, *Phys. Rev.*, 1966, **144**, 39.

⁶⁹ P. G. H. Sandars, *Adv. Chem. Phys.*, 1969, **14**, 365.

⁷⁰ M. B. Johnson and M. Baranger, *Ann. Phys. (N.Y.)*, 1971, **62**, 172.

⁷¹ T. T. S. Kuo, S. Y. Lee, and K. F. Ratcliffe, *Nuclear Phys.*, 1971, **A176**, 65.

⁷² I. Lindgren, *J. Phys. B: Atom. Mol. Phys.*, 1974, **7**, 2441; *Int. J. Quantum Chem. Symp.*, 1978, **12**, 33.

⁷³ B. Levy, in 'Proceedings of the Fourth Seminar on Computational Methods in Quantum Chemistry, 1978', ed. B. Roos and G. H. F. Diercksen, Max-Planck-Institut für Physik und Astrophysik, Munich.

⁷⁴ V. Kvasnicka, *Czech. J. Phys.*, 1974, **B24**, 605; *Adv. Chem. Phys.*, 1977, **36**, 345.

⁷⁵ D. Hegarty and M. A. Robb, *Mol. Phys.*, 1979, **37**, 1455.

⁷⁶ G. Hose and U. Kaldor, *J. Phys. B: Atom. Mol. Phys.*, 1979, **12**, 3827.

The work of Gerratt,⁷⁷ Gallup,⁷⁸ and Goddard⁷⁹ suggests a possible reference function for use in such a scheme, *e.g.* ref. 80. Newman^{81, 82} has examined a many-body perturbative formalism which uses biorthogonal sets of orbitals. The use of non-orthogonal orbitals has also been discussed by Kvasnicka,⁸³ Moshinsky and Seligman,⁸⁴ Gouyet,⁸⁵ Cantu *et al.*,⁸⁶ and Kirtman and Cole.⁸⁷

3 The Algebraic Approximation

General Remarks.—The algebraic approximation is fundamental to most applications of the methods of quantum mechanics to molecules. When employing non-variational techniques, such as perturbation theory, in the study of correlation energies it is important to be very clear about the origin of truncation effects in a particular calculation. In molecular studies using diagrammatic perturbation theory there are, of course, two truncation effects, that arising from basis set restrictions (*i.e.* by invoking the algebraic approximation), and that arising from truncation of the perturbation series. In applications of perturbation theory to molecules, it is important that one does not obtain good results by a fortuitous cancellation of these two sources of error.

In the first part of this section, the relationship between the solution of the Schrödinger equation and the hamiltonian in the space generated by a given basis set is discussed in some detail. Since basis set limitations appear to be one of the largest sources of error in most present day molecular calculations, the concept of a universal even-tempered basis set is discussed in the second part of this section. This concept represents an attempt to overcome the incomplete basis set problem, at least for diatomic molecules. Further aspects of the basis set truncation problem are discussed in the final part of this section.

The Algebraic Approximation.—The determination of the electronic structure of atoms and molecules containing N electrons involves the evaluation of an appropriate eigenvalue and associated eigenfunction of a semi-bounded self-adjoint hamiltonian operator, \mathcal{H} , in Hilbert space \mathcal{h} . A tractable scheme for solving such equations is the algebraic approximation in which eigenfunctions are parameterized by expansion in a finite set of functions. Integro-differential Hartree-Fock equations thus become algebraic equations for the expansion coefficients. The difficulties of the atomic correlation problem are compounded in molecular studies by the impossibility of factorizing the variables in a molecular field and use of the algebraic approximation becomes almost obligatory.

⁷⁷ J. Gerratt, *Adv. Atom. Mol. Phys.*, 1971, **7**, 141; and in 'Theoretical Chemistry', ed. R. N. Dixon (Specialist Periodical Reports), The Chemical Society, London, 1974, Vol. 1, p. 60.

⁷⁸ R. C. Morrison and G. A. Gallup, *J. Chem. Phys.*, 1969, **50**, 1214.

⁷⁹ W. A. Goddard, *Phys. Rev.*, 1967, **157**, 81.

⁸⁰ S. Wilson and J. Gerratt, *Mol. Phys.*, 1975, **30**, 777; S. Wilson, *Mol. Phys.*, 1978, **35**, 1.

⁸¹ D. J. Newman, *J. Phys. Chem. Solids*, 1969, **30**, 1709.

⁸² D. J. Newman, *J. Phys. Chem. Solids*, 1970, **31**, 1143.

⁸³ V. Kvasnicka, *Chem. Phys. Lett.*, 1977, **51**, 165.

⁸⁴ M. Moshinsky and T. H. Seligman, *Ann. Phys. (N.Y.)*, 1971, **66**, 311.

⁸⁵ J. F. Gouyet, *J. Chem. Phys.*, 1973, **59**, 4637.

⁸⁶ A. A. Cantu, D. J. Klein, F. A. Matsen, and T. H. Seligman, *Theor. Chim. Acta*, 1975, **38**, 341.

⁸⁷ B. Kirtman and S. Cole, *J. Chem. Phys.*, 1978, **69**, 5055.

The algebraic approximation results in the restriction of the domain of the operator \mathcal{H} to a finite dimensional subspace, \mathcal{S} , of the Hilbert space \mathcal{H} . The algebraic approximation may be implemented by defining a suitable orthonormal basis set of M ($< N$) one-electron spin orbitals and constructing all unique N -electron determinants $|\mu\rangle$ using the M one-electron functions. The number of unique determinants that can be formed is $\eta = \binom{M}{N}$, and η is the dimension of the subspace \mathcal{S} spanned by the set of determinants. The algebraic approximation restricts the domain of \mathcal{H} to this η -dimensional subspace.

Within the algebraic approximation, the Schrödinger equation may, in principle, be solved by the method of configuration mixing. The wave function is then expressed as a superposition of configurations $|\mu\rangle$ with linear coefficients C_μ , the optimal expansion coefficients determined by the variation principle. In practice, difficulties arise in setting up and solving secular equations of high order. Thus, only a small subset of the $|\mu\rangle$ is usually employed in the expansion.

Diagrammatic many-body perturbation theory may also be formulated within the algebraic approximation. The domain of the perturbation theory operators is restricted to the η -dimensional space spanned by the $|\mu\rangle$ and consequently the perturbation theory wave function is generated in terms of an η -dimensional representation. The results of many-body perturbation theory calculations, when carried through infinite order, are identical to those of configuration mixing if the same basis set, *i.e.* subspace \mathcal{S} , is used in both calculations. However, in practice, the perturbation series must be truncated at some finite order and in this case the degree of agreement with the configuration interaction result is a measure of the convergence of the perturbation series at this order.

Let us briefly discuss the relationship between approaches which use basis sets and thus have a discrete single-particle spectrum and those which employ the Hartree-Fock hamiltonian, which has a continuous spectrum, directly. Consider an atom enclosed in a box of radius R , much greater than the atomic dimension. This replaces the continuous spectrum by a set of closely spaced discrete levels. The relationship between the matrix Hartree-Fock problem, which arises when basis sets of discrete functions are utilized, and the Hartree-Fock problem can be seen by letting the dimensions of the box increase to infinity. Calculations which use discrete basis sets are thus capable, in principle, of yielding exact expectation values of the hamiltonian and other operators. In using a discrete basis set, we replace integrals over the continuum which arise in the evaluation of expectation values by summations. The use of a discrete basis set may thus be regarded as a quadrature scheme.

Once the algebraic approximation has been invoked there is essentially no difference between the atomic problem and the molecular problem, except that the multicentre integrals which arise in the latter case are more difficult to evaluate.

Universal Basis Sets.—Historically, it has been necessary to restrict the size of basis sets employed in molecular calculations to a reasonably small number of functions in order to keep the computation tractable. However, to achieve high accuracy, moderately large basis sets are ultimately required, especially if a significant fraction of the molecular correlation energy is to be recovered. Since

the flexibility of a basis set generally increases as the number of functions is increased, the need to optimize parameters becomes less important. This has led to the suggestion that a single moderately large basis set, with a reasonable choice of parameters, might be suitable for a variety of systems. Such a basis set has been termed a 'universal basis set'.⁸⁸⁻⁹²

It has been shown that Slater type orbitals restricted to $1s, 2p, 3d, \dots$ functions can lead to good results for total energies. Orbital exponents, ζ , may be chosen by the 'even-tempered' formula⁸⁸⁻⁹²

$$\zeta_k = \alpha\beta^{k-1} \quad k = 1, 2, \dots, M \quad (59)$$

It can be shown that the metric matrix, S , then has the property

$$S_{i,j} = S_{i+1,j+1} \quad (60)$$

The parameters α , β , and M for the universal even-tempered basis set thus generated have been chosen quite arbitrarily using the following guidelines:

- (i) α must be small enough to ensure a wide range of orbital exponent values,
- (ii) β must be large enough to avoid possible near linear dependence,
- (iii) M must be large enough to generate a 'near complete' set.

The following values of α , β , and M have been shown to be useful in studies of atoms and diatomic molecules:⁸⁸⁻⁹²

$$\begin{aligned} 1s: & \alpha = 0.5 \quad \beta = 1.55 \quad M = 9 \\ 2p: & \alpha = 1.0 \quad \beta = 1.60 \quad M = 6 \\ 3d: & \alpha = 1.5 \quad \beta = 1.65 \quad M = 3 \end{aligned} \quad (61)$$

Thus the orbital exponents of the $1s$ functions range from 0.5 to 16.7 bohr^{-1} , the $2p$ exponents range from 1.0 to 10.5 bohr^{-1} , and the $3d$ exponents from 1.5 to 4.1 bohr^{-1} . The energy is generally found to be more sensitive to the particular choice of β than the choice of α .

Universal even-tempered basis sets have been employed in calculations on first-row and second-row atoms using the matrix Hartree-Fock model.^{88,89} Atomic calculations including electron correlation have also been reported.⁹⁰ For molecules calculations using universal even-tempered basis sets of s, p , and d functions have been reported at both the Hartree-Fock level⁹¹ and including correlation.⁹² For the nitrogen, carbon monoxide, and boron fluoride molecules about 80% of the empirical correlation energy is recovered by taking the perturbation series through third-order.

⁸⁸ D. M. Silver, S. Wilson, and W. C. Nieuwpoort, *Int. J. Quantum Chem.*, 1978, **14**, 635.

⁸⁹ D. M. Silver and W. C. Nieuwpoort, *Chem. Phys. Lett.*, 1978, **57**, 421.

⁹⁰ D. M. Silver and S. Wilson, *J. Chem. Phys.*, 1978, **69**, 3787.

⁹¹ S. Wilson and D. M. Silver, *Chem. Phys. Lett.*, 1979, **63**, 367.

⁹² S. Wilson and D. M. Silver, *J. Chem. Phys.*, 1980, **72**, 2159; unpublished work.

⁹³ C. M. Reeves and J. Harrison, *J. Chem. Phys.*, 1963, **39**, 11.

⁹⁴ K. Ruedenberg, R. C. Raffanetti, and R. D. Bardo, in 'Energy Structure and Reactivity', Proceedings of the 1972 Boulder Conference on Theoretical Chemistry, Wiley, New York 1973.

⁹⁵ R. C. Raffanetti, *J. Chem. Phys.*, 1973, **59**, 5936.

⁹⁶ R. D. Bardo and K. Ruedenberg, *J. Chem. Phys.*, 1973, **59**, 5956, 5966.

⁹⁷ R. C. Raffanetti and K. Ruedenberg, *J. Chem. Phys.*, 1973, **59**, 5978.

⁹⁸ R. D. Bardo and K. Ruedenberg, *J. Chem. Phys.*, 1974, **60**, 918.

⁹⁹ R. C. Raffanetti, *Int. J. Quantum Chem. Symp.*, 1975, **9**, 289.

Let us comment at this point on the use of the even-tempered method for generating orbital exponents. A universal basis set clearly need not be an even-tempered one. However, even-tempered basis functions do span the one-electron space in a fairly uniform fashion. Unlike a set of exponents determined by energy optimization for a particular system, we expect that the even-tempered functions will be more suitable for transferring between systems. Even-tempered orbital exponents are defined through the recursion

$$\zeta_{k+1} = \zeta_k \beta \quad (62)$$

A possibly useful generalization of this formula is the recursion

$$\zeta_{k+1} = \zeta_k (\beta + k\gamma) \quad (63)$$

where γ is an additional parameter.

Several advantages would accrue to the use of a universal basis set. Since most electronic structure studies of molecules begin with the valuation of one-electron and two-electron integrals over the primitive basis functions, then, for a given set of nuclear positions, these integrals could be computed once and used for all subsequent studies without regard to the identity of the constituent atoms. This transferability extends, of course, to all integrals including multicentre two-electron integrals. In order to be an acceptable concept, the universal basis set must be capable of providing a uniform description of a series of atoms. Since such a basis set is necessarily moderately large, it should yield reasonably high accuracy as well as uniformity.

The concept of a universal gaussian basis set should be briefly discussed since gaussian functions are widely used in molecular studies, especially in studies of polyatomic systems. Clearly, gaussian basis sets could be transferred from molecule to molecule in precisely the manner we have demonstrated for Slater functions. However, it is generally accepted that Slater basis functions provide a more realistic description of the orbitals especially near nuclei. Integrals over universal basis sets are generated once and stored for future use and it would therefore seem more profitable to use Slater functions which would generate a smaller integral list, especially if a significant fraction of the correlation energy is to be recovered. Raffanetti⁹⁹ has investigated the use of even-tempered gaussian basis sets. His results demonstrate the inferior nature of gaussian functions in accurate work. However, it should be noted that multicentre integrals over gaussian functions can be evaluated with greater precision than integrals over Slater functions.

It should be noted that the concept of a universal basis set could prove useful in almost all molecular studies in which finite basis sets are employed, *e.g.* electron-molecule scattering. Such basis sets lead to accurate results because they are moderately large. Furthermore, they afford a certain degree of uniformity in that they are not optimized for one particular property.

Basis Set Truncation.—Basis set truncation does appear to be one of the main sources of error in the majority of calculations on small molecules. The efficiency of algorithms based on the diagrammatic perturbation expansion will allow increasingly large basis sets to be employed in molecular studies during the next few years.

Calculations for atomic systems have shown that almost all of the correlation energy may be recovered in second-order, if there are no near-degeneracy effects in the reference spectrum, when a sufficiently large basis set is employed. For the ground state of the neon atom, Eggarter and Eggarter¹⁰⁰⁻¹⁰³ have shown that 98% of the empirical correlation energy can be recovered by including functions with l quantum number up to 6 in the basis set. Since there is essentially no difference between the atomic and the molecular problems once a finite basis set is introduced (excepting the difficulty of evaluating the multicentre integrals, of course), it is expected that similar results will be obtained for molecules once sufficiently large basis sets are utilized.

In order to discuss the convergence of atomic and molecular calculations with respect to basis set size, one must have an orderly procedure for extending the basis set. This is necessary if the relationship between various restricted basis sets and complete bases is to be understood. The recent work of Ruedenberg and his co-workers^{104,105} is of great interest in this respect. They have examined the effective convergence of orbital bases through systematic sequences of gaussian primitives. They develop various sets of even-tempered gaussian functions-such that

$$\alpha = \alpha(M) \quad (64)$$

and

$$\beta = \beta(M) \quad (65)$$

where

$$\alpha(M) \rightarrow 0 \quad \beta(M) \rightarrow 1 \quad [\beta(M)]^M \rightarrow \infty \quad (66)$$

as

$$M \rightarrow \infty \quad (67)$$

Clearly, this approach can also be used in the case of Slater basis sets and, moreover, in the case of universal Slater basis sets. Ruedenberg and co-workers^{104,105} have shown that, within the molecular orbital approximation, this systematic approach gives a series of energy values which smoothly approach the Hartree-Fock limit. Similarly smooth convergence is to be expected in the calculation of correlated wave functions and expectation values, and will be the subject of future studies in this area.¹⁰⁶

4 Truncation of the Many-body Perturbation Expansion

General Remarks.—Perturbation theory forms the basis of a unique approach to the calculation of accurate expectation values in that it provides a clearly defined order parameter indicating the relative importance of various terms. This order

¹⁰⁰ E. Eggarter and T. P. Eggarter, *J. Phys. B: Atom. Mol. Phys.*, 1978, **11**, 1157.

¹⁰¹ E. Eggarter and T. P. Eggarter, *J. Phys. B: Atom. Mol. Phys.*, 1978, **11**, 2069.

¹⁰² E. Eggarter and T. P. Eggarter, *J. Phys. B: Atom. Mol. Phys.*, 1978, **11**, 2969.

¹⁰³ T. P. Eggarter and E. Eggarter, *J. Phys. B: Atom. Mol. Phys.*, 1978, **11**, 3635.

¹⁰⁴ D. F. Feller and K. Ruedenberg, *Theor. Chim. Acta*, 1979, **52**, 231.

¹⁰⁵ M. Schmidt and K. Ruedenberg, *J. Chem. Phys.*, 1979, **71**, 3951.

¹⁰⁶ S. Wilson, *Theor. Chim. Acta*, 1980, **57**, 53; *ibid.*, 1980, **58**, 31; *ibid.*, 1981, in the press.

parameter provides an unambiguous criterion for truncating expansions for expectation values. Brandow¹⁰⁷ thus comments that perturbation theory 'seems to be the "least biased" of all the many-body techniques'.

In this section various aspects of the truncation of the perturbation expansion are discussed. The use of Padé approximants in perturbation theory is outlined and the special invariance properties of the $[N+1/N]$ Padé approximants in Rayleigh-Schrödinger perturbation theory are emphasized. Scaling of the zero-order hamiltonian is considered and the construction of upper bounds to the energy described. Fourth-order and higher-order terms are presented and discussed in some detail. Investigations of the effects of quasi-degeneracy on the convergence properties of the perturbation series are reviewed. Finally, since most other approaches to the electron correlation problem in molecules may be regarded as different ways of truncating the many-body perturbation series, a brief description of the relationship between many-body perturbation theory and some other methods is given.

Padé Approximants and Perturbation Expansions.—The $[P/Q]$ Padé approximant^{108,109} to a Taylor series $T(x)$ of order M is defined by

$$[P/Q](x) = \mathcal{P}(x)/\mathcal{Q}(x); \quad P + Q = M \quad (68)$$

where \mathcal{P} is a polynomial of order P and \mathcal{Q} is a polynomial of order Q such that

$$\mathcal{P}(x) - \mathcal{Q}(x)[P/Q](x) = \mathcal{O}(x^{M+1}) \quad (69)$$

where $\mathcal{O}(x^{M+1})$ denotes terms of order $M+1$ and higher.

Padé approximants provide a useful representation of perturbation series. They often converge when the usual power series diverges. Unlike the power series, Padé approximants can handle a class of function with various types of singularities still providing correct uniform convergence.¹⁰⁹ In the Lennard-Jones Brillouin Wigner perturbation theory, Padé approximants can be used to find bounds to the exact energy.¹¹⁰ On the other hand, in Rayleigh-Schrödinger perturbation theory, the $[N+1/N]$ Padé approximants are special^{111,112} in that, when the expansion parameter is set equal to unity, the numerical value of this approximant is invariant to two modifications in the zero-order hamiltonian operator, namely a change of scale and a shift of origin.

Let us consider these two modifications of a given zero-order operator, \mathcal{H}_0 ; that is a uniform displacement of the zero-order energy spectrum and a uniform change of scale in the spacing of the zero-order energy levels. Consider the zero-order operator

$$\mathcal{H}_0^{\mu,\nu} = \mu\mathcal{H}_0 + \nu\hat{I} \quad (70)$$

where \hat{I} is the identity operator and μ and ν are scalars. The corresponding perturbation operator is

$$\mathcal{H}_1^{\mu,\nu} = \mathcal{H}_1 + (1-\mu)\mathcal{H}_0 - \nu\hat{I} \quad (71)$$

¹⁰⁷ B. H. Brandow, in 'Effective Interactions and Operators in Nuclei', ed. B. R. Barratt, Springer-Verlag, Berlin, 1975.

¹⁰⁸ H. Padé, *Ann. sci. Ecol. norm. sup. Paris (Suppl.)*, 1892, 9, 3.

¹⁰⁹ G. A. Baker, 'Essentials of Padé Approximants', Academic Press, New York, 1975.

¹¹⁰ O. Goscinski, *Int. J. Quantum Chem.*, 1967, 1, 769.

¹¹¹ S. Wilson, D. M. Silver, and R. A. Farrell, *Proc. R. Soc. London, Ser. A*, 1977, 356, 363.

¹¹² E. Feenberg, *Ann. Phys. (N.Y.)*, 1958, 3, 292.

Note that when the perturbation parameter is put equal to unity the total hamiltonian operator is recovered, *i.e.*

$$\mathcal{H} = (\mathcal{H}_0^{\mu,\nu} + \lambda \mathcal{H}_1^{\mu,\nu})_{\lambda=1} \quad (72)$$

The energy coefficients, $E_i^{\mu,\nu}$, where i denotes the order of perturbation, may be related to the values of $E_i^{1,0}$ by the expressions

$$E_0^{\mu,\nu} = \mu E_0^{1,0} + \nu \quad (73)$$

$$E_1^{\mu,\nu} = E_1^{1,0} + (1-\mu) E_1^{1,0} - \nu \quad (74)$$

and

$$E_n^{\mu,\nu} = \frac{1}{\mu^{n-1}} \sum_{k=2}^{k=n} \binom{n-2}{k-2} (\mu-1)^{n-k} E_k^{0,0} \quad n = 2, 3, \dots \quad (75)$$

It can be shown¹¹¹ that the $[N+1/N]$ Padé approximants alone among all Padé approximants of order $2N+1$ are invariant to an arbitrary choice of μ and ν , when λ is set to unity.

The $[N+1/N]$ Padé approximants to the energy series also have the advantage that they have a linear dependence on the perturbation parameter, λ , as it becomes large. Furthermore, the Goldstone level shift formula¹¹ may be written

$$\Delta E_0 = \langle \Phi_0 | \mathcal{H}_1 \hat{U} | \Phi_0 \rangle_L \quad (76)$$

where the evolution operator, \hat{U} , is unitary if all terms are included but not if the expansion is truncated. A unitary approximation to \hat{U} can be obtained by forming the $[N/N]$ operator Padé approximant.¹¹³ This has the same form as a function of the perturbation parameter as the $[N+1/N]$ scalar Padé approximant to the level shift.

From third-order perturbation calculations, the $[2/1]$ Padé approximants can be formed. Several additional reasons can be advanced for their use:

(i) there is a large amount of evidence demonstrating that this leads to improved results,¹¹⁴

(ii) this may be regarded as the choice of scaling parameter which makes the third-order energy vanish,¹¹⁵⁻¹¹⁷

(iii) it may also be regarded as the energy expression for which the energy is a minimum with respect to choice of scaling parameter.¹¹⁸

It should be noted that for one-electron properties, such as dipole moments, the $[N/N]$ Padé approximants are invariant to changes of scale and shifts of origin in the reference spectrum⁸ whereas for second-order properties, such as polarizabilities, the $[N/N+1]$ Padé approximants are to be preferred. Indeed, for polarizabilities the use of the form

$$\alpha_0 \left(1 - \frac{\alpha_1}{\alpha_0} \right)^{-1} \quad (77)$$

has been advocated by a number of authors.^{8, 119, 120}

¹¹³ J. L. Gammel and F. A. McDonald, *Phys. Rev.*, 1966, **142**, 1245.

¹¹⁴ S. Wilson, *J. Phys. B: Atom. Mol. Phys.*, 1979, **12**, 1623.

¹¹⁵ A. T. Amos, *J. Chem. Phys.*, 1970, **52**, 603.

¹¹⁶ A. T. Amos, *Int. J. Quantum Chem.*, 1972, **6**, 125.

¹¹⁷ A. T. Amos, *J. Phys. B: Atom. Mol. Phys.*, 1978, **11**, 2053.

¹¹⁸ D. T. Tuan, *Chem. Phys. Lett.*, 1970, **7**, 115.

Padé approximants to perturbation series have been considered by numerous authors,¹²¹ particularly those interested in effective interactions in nuclei. They have been used in studies of the 'intruder state' problem which can arise when a multideterminantal function is used as a reference in a perturbative scheme.¹²²

Scaling of the Zero-order Hamiltonian.—It has been demonstrated^{123–125} that improved results can be obtained from second-order Rayleigh–Schrödinger perturbation studies of electron correlation energies using very large basis sets by introducing a scaling parameter, μ , in the zero-order hamiltonian, \mathcal{H}_0 . The scaling parameter may be determined, from calculations taken to third-order in the energy and using a basis set of moderate size, by imposing the condition that the third-order energy coefficient corresponding to the zero-order operator, $\mu\mathcal{H}_0$, be zero. The correlation energy is then approximated by $\mu^{-1}E_2$, where E_2 is the second-order energy resulting from the calculation using the large basis set.

Second-order calculations with large basis sets are computationally tractable. One of the most time consuming parts of many calculations is the transformation of the two-electron integrals over atomic functions to integrals over molecular orbitals. For second-order calculations only a restricted list of two-electron integrals is required (although the restricted transformation is still an n^5 process, where n is the number of basis functions). It is envisaged that the concept of a universal even-tempered basis set will prove useful in developing the large basis sets required for these calculations.^{88–92} The scaling of the zero-order hamiltonian is also useful in the calculation of molecular properties and has been demonstrated¹²⁰ for the polarizability of the hydrogen molecule.^{126, 127}

Modified Potentials.—It is possible to modify the perturbation series by using alternative potentials in the zero-order hamiltonian. The modified potential

$$V^{N-1}(r_1) = \sum_{k=1}^{N-1} \int dr_2 \phi^*(r_2) r_{12}^{-1} (1 - P_{12}) \phi_k(r_2) \quad (78)$$

has been widely used in atomic studies.⁵ Recent calculations^{128, 129} on the hydrogen fluoride molecule have indicated that there is little difference between results obtained using the Hartree–Fock potential and the above modified potential when *all* terms are included through third-order. For the FH molecule using unshifted denominators, 80.2% of the empirical correlation energy was

¹¹⁹ G. Howat, M. Trsic, and O. Goscinski, *Int. J. Quantum Chem.*, 1977, **11**, 283.

¹²⁰ S. Wilson, *Mol. Phys.*, 1980, **39**, 525; S. Wilson and A. J. Sadley, to be published.

¹²¹ G. A. Baker, *Adv. Theor. Phys.*, 1965, **1**, 1; O. Goscinski and E. Brandas, *Phys. Rev. A*, 1970, **1**, 552.

¹²² E. M. Krenciglowa and T. T. S. Kuo, *Nuclear Phys.*, 1974, **A235**, 171; H. M. Hoffmann, S. Y. Lee, J. Richert, and H. A. Weidenmuller, *Ann. Phys.*, 1974, **85**, 410; J. M. Leinaas and T. T. S. Kuo, *Ann. Phys.*, 1978, **111**, 19; T. H. Schucan and H. A. Weidenmuller, *Ann. Phys.*, 1972, **73**, 108; J. Richert, T. H. Schucan, M. H. Scrubel, and H. A. Weidenmuller, *Ann. Phys.*, 1976, **96**, 139; T. H. Schucan and H. A. Weidenmuller, *Ann. Phys.*, 1973, **76**, 483.

¹²³ S. Wilson, *J. Phys. B: Atom. Mol. Phys.*, 1979, **12**, L135.

¹²⁴ F. W. Byron and C. J. Joachain, *J. Phys. B: Atom. Mol. Phys.*, 1979, **12**, L597.

¹²⁵ S. Wilson, *J. Phys. B: Atom. Mol. Phys.*, 1979, **12**, L599.

¹²⁶ T. Itagaki and A. Saika, *Chem. Phys. Lett.*, 1977, **52**, 530.

¹²⁷ T. Itagaki and A. Saika, *J. Chem. Phys.*, 1979, **70**, 2378.

¹²⁸ D. M. Silver and R. J. Bartlett, *Phys. Rev. A*, 1976, **13**, 1.

¹²⁹ D. M. Silver, S. Wilson, and R. J. Bartlett, *Phys. Rev. A*, 1977, **16**, 477.

recovered in second-order when the Hartree-Fock potential was employed, whereas 101.2% of the correlation energy was recovered when the V^{N-1} modified potential was used. The [2/1] Padé approximant to the perturbation series using the Hartree-Fock potential gave 79.6% of the correlation, which is close to the 77.8% given by the [2/1] Padé approximant to the series based on the modified potential. The infinite-order result should, of course, be independent of the choice of zero-order hamiltonian.

Upper Bounds to Total Energies.—In performing a calculation of the energy to third-order one also implicitly calculates the wave function to first-order. Let the wave function through first-order be written as

$$\Phi_0 + \lambda \Phi_1 \quad (79)$$

where the parameter λ has been introduced. The truncated expansion for the energy is not bounded: however by substituting the first-order wave function in the Rayleigh quotient, an upper bound is obtained. This may be written as³²

$$E_{\text{var}}(\lambda) = E_0 + E_1 + \frac{(2\lambda - \lambda^2)E_2 + \lambda^2 E_3}{1 + \lambda^2 \Delta_{11}} \quad (80)$$

where the overlap integral, Δ_{11} , is given by

$$\Delta_{11} = \frac{1}{4} \sum_{ij} \sum_{ab} \left(\frac{\mathcal{J}_{ijab}}{\mathcal{D}_{ijab}} \right)^2 \quad (81)$$

λ may be regarded as a variational parameter. Its optimal value may be obtained by invoking the variation principle, giving

$$\lambda_{\text{opt}} = \Delta_{11}^{-1} [\sqrt{\zeta^2 + \Delta_{11}} - \zeta] \quad (82)$$

where

$$\zeta = \frac{1}{2} (1 - E_3/E_2) \quad (83)$$

Unfortunately, by forming an upper bound one introduces terms depending on the square of the number of electrons and thus the quality of this upper bound deteriorates as the number of electrons is increased. This is illustrated in Table 1 for an array of well-separated nitrogen molecules.

Table 1 Size-consistency error in an array of well separated N_2 Molecules†

m	n^a	$E_2 \Delta_{11}^b$	e^c
1	14	0.00	-0.45
2	28	0.09 (10%)	-0.90
3	42	0.30 (22%)	-1.35
4	56	0.59 (33%)	-1.80
5	70	1.00 (44%)	-2.25

†Based on results given in ref. 92.

^a Number of electrons. ^b Fourth-order size-consistency error; percentage of estimated correlation energy given in parentheses. ^c Estimated correlation energy.

Fourth-order and Higher-order Terms.—Most methods currently employed in the study of electron correlation in atoms and molecules, for example the coupled-electron pair theory, limited configuration mixing, *etc.*, may be regarded as third-

order theories in that they neglect or approximate fourth-order and higher-order terms in the perturbation analysis of the energy. Diagrammatic many-body perturbation theory offers a systematic scheme for extending such calculations. The perturbation series forms the basis of a balanced treatment of the correlation problem in that it provides a clearly defined order parameter which indicates the relative importance of various terms. There is considerable interest in the evaluation of the fourth-order terms in the many-body perturbative expansion since these terms represent, at least in part, the dominant corrections to most techniques currently being employed in calculating atomic and molecular correlation energies.

Unlike the second-order and third-order energy diagrams, the fourth-order diagrams can involve intermediate states which are singly-excited, doubly-excited, triply-excited, and quadruply-excited with respect to the Hartree-Fock reference function.^{8, 130}

There are four diagrams, using the Bradow convention⁵¹ which involve an intermediate state which is singly-excited with respect to the Hartree-Fock function, these are shown in Figure 5. Diagrams A_S and D_S are related by time reversal, whereas B_S and C_S are related by complex conjugation.¹³⁰

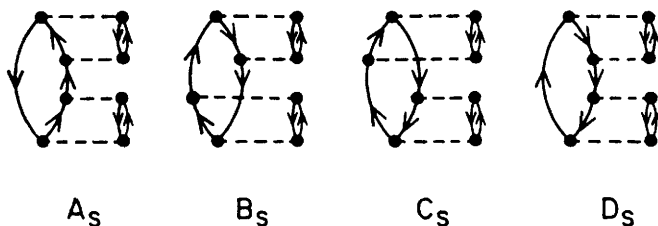


Figure 5 Fourth-order diagrams which involve singly-excited intermediate states

The twelve diagrams of the fourth-order which involve only doubly-excited intermediate states are displayed in Figure 6. Diagrams (B_D, C_D) , (E_D, F_D) , and (G_D, H_D) are related by complex conjugation. Diagrams (A_D, D_D) , (E_D, H_D) , (F_D, G_D) , and (J_D, K_D) are related by time reversal.

The diagrams which involve a triply-excited intermediate state in fourth-order are shown in Figure 7. Explicitly, diagrams A_T , B_T , C_T , and D_T , for example, correspond to the expressions

$$E_4(A_T) = -\frac{1}{2} \sum (\mathcal{J}_{ijab} \mathcal{J}_{akcd} \mathcal{J}_{cbek} \mathcal{J}_{edij}) / (\mathcal{D}_{ijab} \mathcal{D}_{ijkbcd} \mathcal{D}_{ijde}) \quad (84)$$

$$E_4(B_T) = -\frac{1}{2} \sum (\mathcal{J}_{ijab} \mathcal{J}_{akcd} \mathcal{J}_{cdkj} \mathcal{J}_{ebik}) / (\mathcal{D}_{ijab} \mathcal{D}_{ijkbcd} \mathcal{D}_{ikbe}) \quad (85)$$

$$E_4(C_T) = -\frac{1}{2} \sum (\mathcal{J}_{ijab} \mathcal{J}_{klte} \mathcal{J}_{mbkl} \mathcal{J}_{acmj}) / (\mathcal{D}_{ijab} \mathcal{D}_{jklabc} \mathcal{D}_{jmac}) \quad (86)$$

$$E_4(D_T) = -\frac{1}{2} \sum (\mathcal{J}_{ijab} \mathcal{J}_{klte} \mathcal{J}_{mckj} \mathcal{J}_{abml}) / (\mathcal{D}_{ijab} \mathcal{D}_{jklabc} \mathcal{D}_{emab}) \quad (87)$$

Time-reversal symmetry can be seen to relate diagrams A_T , B_T , E_T , and F_T to diagrams D_T , C_T , H_T , and G_T , respectively. Diagrams (I_T, L_T) and (J_T, K_T) form complex conjugate pairs. Diagrams (M_T, P_T) and (N_T, O_T) are related by time reversal and (M_T, N_T) and (O_T, P_T) are complex conjugates.

¹³⁰ S. Wilson and D. M. Silver, *Int. J. Quantum Chem.*, 1979, 15, 683.

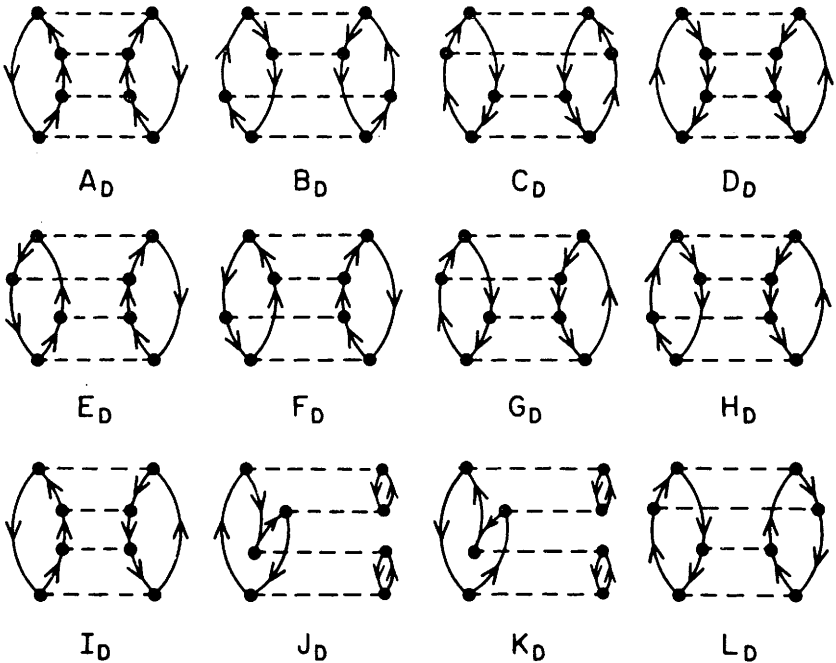


Figure 6 Fourth-order diagrams which involve doubly-excited intermediate states

Finally, there are seven fourth-order terms which involve an intermediate state which is quadruply-excited with respect to the Hartree-Fock reference function. These diagrams are shown in Figure 8. Time reversal relates diagrams (B_Q, C_Q), (D_Q, G_Q), and (E_Q, F_Q). Explicitly, diagrams A_Q, B_Q, and C_Q, for example, correspond to the expressions

$$E_4(A_Q) = \sum_{ijkl} \sum_{abcd} (\mathcal{I}_{ijab} \mathcal{I}_{klcd} \mathcal{I}_{cbil} \mathcal{I}_{adkj}) / (\mathcal{D}_{ijab} \mathcal{D}_{ijklabcd} \mathcal{D}_{kjad}) \quad (88)$$

$$E_4(B_Q) = \frac{1}{16} \sum_{ijkl} \sum_{abcd} (\mathcal{I}_{ijab} \mathcal{I}_{klcd} \mathcal{I}_{cdij} \mathcal{I}_{abki}) / (\mathcal{D}_{ijab} \mathcal{D}_{ijklabcd} \mathcal{D}_{klab}) \quad (89)$$

$$E_4(C_Q) = \frac{1}{16} \sum_{ijkl} \sum_{abcd} (\mathcal{I}_{ijab} \mathcal{I}_{klcd} \mathcal{I}_{abki} \mathcal{I}_{cdij}) / (\mathcal{D}_{ijab} \mathcal{D}_{ijklabcd} \mathcal{D}_{ijcd}) \quad (90)$$

The fourth-order quadruple-excitation energy diagrams arise from the disconnected wave function diagrams shown in Figure 9. This observation leads to considerable simplification in the evaluation of this energy component. For example, using the identity

$$(\mathcal{D}_{ijab} \mathcal{D}_{ijklabcd} \mathcal{D}_{ijcd})^{-1} + (\mathcal{D}_{ijab} \mathcal{D}_{ijklabcd} \mathcal{D}_{klab})^{-1} = (\mathcal{D}_{ijab} \mathcal{D}_{ijcd} \mathcal{D}_{klab})^{-1} \quad (91)$$

the sum of the energy components corresponding to diagrams B_Q and C_Q may be written as

$$E_4(B_Q + C_Q) = \frac{1}{16} \sum (\mathcal{I}_{ijab} \mathcal{I}_{klcd} \mathcal{I}_{cdij} \mathcal{I}_{abki}) / (\mathcal{D}_{ijab} \mathcal{D}_{ijcd} \mathcal{D}_{klab}) \quad (92)$$

It should be noted that this simplification does not occur when the shifted, or

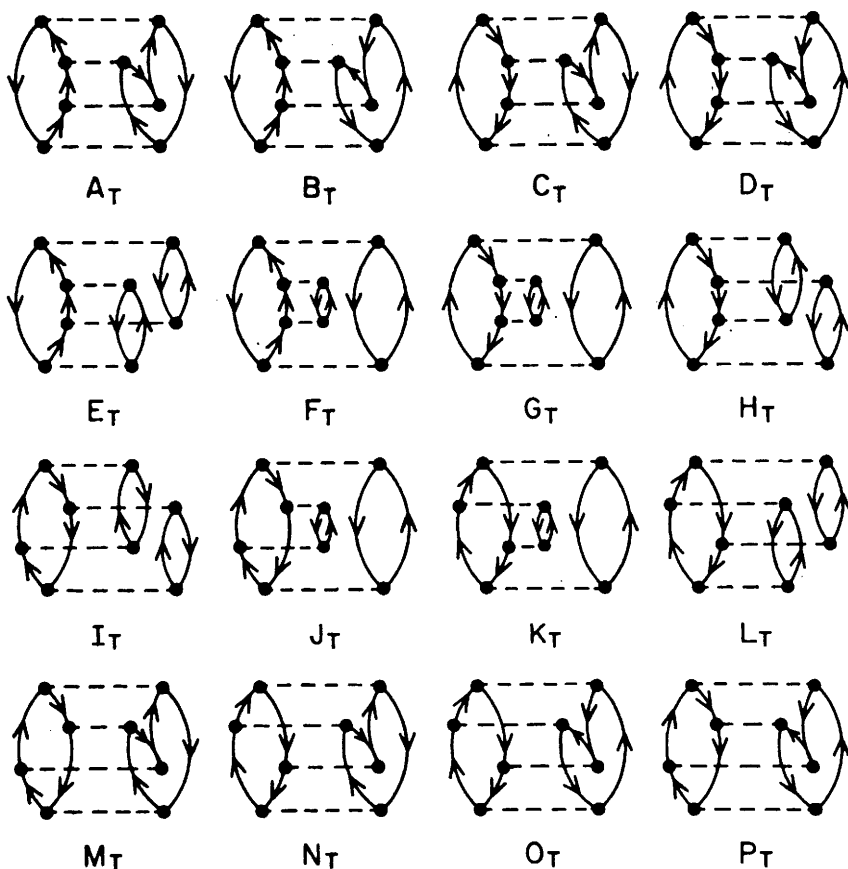


Figure 7 Fourth-order diagrams which involve triply-excited intermediate states

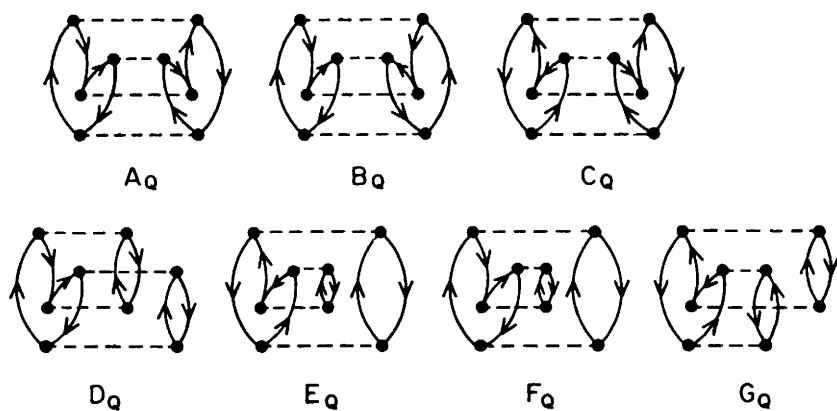


Figure 8 Fourth-order diagrams which involve quadruply-excited intermediate states

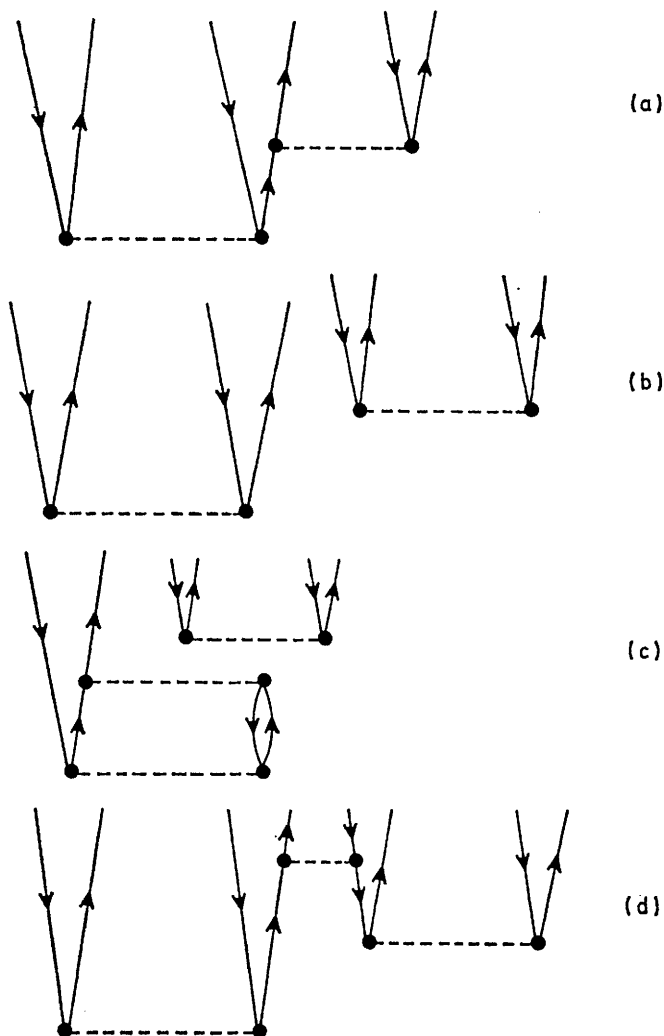


Figure 9 Connected and disconnected wave function diagrams: (a) second-order connected triple-excitation diagram, (b) second-order disconnected quadruple-excitation diagram, (c) third-order disconnected triple-excitation diagram, (d) third-order connected quadruple-excitation diagram

Epstein–Nesbet, perturbation scheme is used. All of the quadruple-excitation terms may be written in the form

$$M \sum_{\mu} f_{\mu} g_{\mu} \quad (93)$$

where

$$f_{\mu} = \sum_{\nu} \frac{\mathcal{I}_{p_1 q_1 r_1 s_1} \mathcal{I}_{p_2 q_2 r_2 s_2}}{\mathcal{D}_{p_2 q_2 c_2 b_2}} \quad (94)$$

and

$$g_{\mu} = \sum_{\nu} \frac{\mathcal{F}_{p_1 q_1 r_1 s_1} \mathcal{F}_{p_2 q_2 r_2 s_2}}{\mathcal{D}_{p_1 q_1 r_1 s_1} \mathcal{D}_{p_2 q_2 r_2 s_2}} \quad (95)$$

M is a constant. μ and ν denote compound indices representing a maximum of four actual indices. The intermediates f_{μ} and g_{μ} differ only in that in the latter there is an additional denominator factor. A number of calculations of the quadruple-excitation component of the fourth-order energy have been reported.¹³¹⁻¹⁴⁰

The triple-excitation fourth-order energy, in contrast to the quadruple-excitation component, arises from connected wave function diagrams. The algorithm required to evaluate this energy component is considerably less tractable than that for the quadruple-excitation energy, depending on n^7 , where n is the number of basis functions. The triple-excitation diagrams can be written in terms of the intermediates.

$$f_{ijk;abc} = \sum_d \frac{\mathcal{F}_{ijab} \mathcal{F}_{dkae}}{\mathcal{D}_{ijab}} \quad (96)$$

and

$$g_{ijk;abc} = \sum_l \frac{\mathcal{F}_{jlba} \mathcal{F}_{ikle}}{\mathcal{D}_{jlba}} \quad (97)$$

Diagrams A_T , B_T , C_T , and D_T correspond to the expressions

$$E_4(A_T) = -\frac{1}{2} \sum \sum f_{ijk;abc} f_{ijk;acb} / \mathcal{D}_{ijkabc} \quad (98)$$

$$E_4(B_T) = -\frac{1}{2} \sum \sum f_{ijk;abc} f_{ikj;abc} / \mathcal{D}_{ijkabc} \quad (99)$$

$$E_4(C_T) = -\frac{1}{2} \sum \sum g_{ijk;abc} g_{ijk;acb} / \mathcal{D}_{ijkabc} \quad (100)$$

$$E_4(D_T) = -\frac{1}{2} \sum \sum g_{ijk;abc} g_{ikj;abc} / \mathcal{D}_{ijkabc} \quad (101)$$

The computation of these energy components has been rendered reasonably tractable by

- (i) using a spin-free formalism;
- (ii) recognizing certain permutational symmetry properties of the intermediates $f_{ijk;abc}$ and $g_{ijk;abc}$;

¹³¹ S. Wilson and D. M. Silver, in 'Proceedings of the Fourth Seminar on Computational Problems in Quantum Chemistry', ed. B. Roos and G. H. F. Diercksen, Max-Planck-Institute für Physik und Astrophysik, Munich, 1978.

¹³² S. Wilson and D. M. Silver, *Mol. Phys.*, 1978, **36**, 1539.

¹³³ S. Wilson and D. M. Silver, *Comput. Phys. Comm.*, 1979, **17**, 47.

¹³⁴ R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.*, 1978, **14**, 91; R. Krishnan, M. J. Frisch, and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 4244; M. J. Frisch, R. Krishnan, and J. A. Pople, *Chem. Phys. Lett.*, 1980, **75**, 66.

¹³⁵ L. T. Redmon, G. D. Purvis, and R. J. Bartlett, *J. Chem. Phys.*, 1978, **69**, 5386.

¹³⁶ R. J. Bartlett, I. Shavitt, and G. D. Purvis, *J. Chem. Phys.*, 1979, **71**, 281.

¹³⁷ I. Hubač, M. Urban, and V. Kellö, *Chem. Phys. Lett.*, 1979, **62**, 584; M. Urban, I. Hubač, V. Kellö, and J. Noga, *J. Chem. Phys.*, 1980, **72**, 3378.

¹³⁸ S. Wilson and V. R. Saunders, *J. Phys. B: Atom. Mol. Phys.*, 1979, **12**, L403; corrigenda, 1980, **13**, 1505; M. F. Guest, and S. Wilson, *Chem. Phys. Lett.*, 1980, **72**, 49; S. Wilson and M. F. Guest, *ibid.*, 1980, **73**, 607.

¹³⁹ V. Kvasnička, V. Laurinc, and S. Biskupič, *Chem. Phys. Lett.*, 1979, **67**, 81.

¹⁴⁰ D. M. Silver, S. Wilson, and C. F. Bunge, *Phys. Rev.*, 1979, **A19**, 1375.

(iii) using a vector-processing computer.

Again a number of calculations of the triple-excitation component of the correlation energy have been reported.^{138,139,141}

Disconnected triple-excitation wave function diagrams and connected quadruple-excitation diagrams first contribute to the energy in fifth-order. A full set of fifth-order diagrams, using the notation of Paldus and Wong^{142,143} for the sake of brevity, is given in Figure 10.⁹ Calculations through fifth-order would enable [3/2] Padé approximants to the energy series to be constructed and variational upper bounds calculated from second-order wave functions. Full fifth-order calculations do not appear to be possible at present. However, the

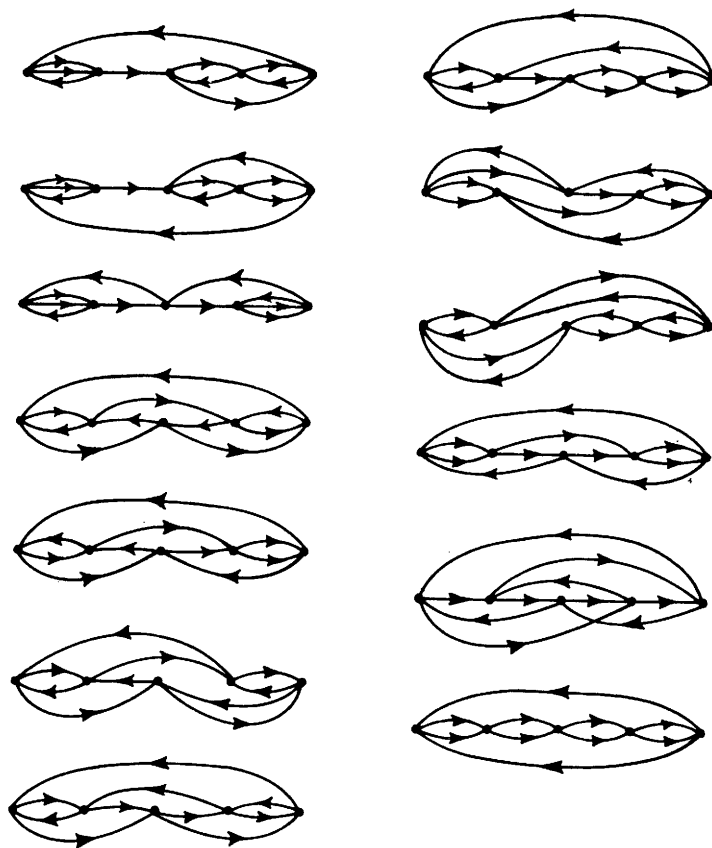


Figure 10 Fifth-order diagrams, using the modified Hugenholtz notation of Paldus and Wong

¹⁴¹ S. Wilson and V. R. Saunders, *Comput. Phys. Comm.*, 1980, **19**, 293.

¹⁴² J. Paldus and H. C. Wong, *Comput. Phys. Comm.*, 1973, **6**, 1.

¹⁴³ H. C. Wong and J. Paldus, *Comput. Phys. Comm.*, 1973, **6**, 9.

recent work by Kvasnička *et al.*¹⁴⁴ on Wigner's $(2n+1)$ rule in many-body perturbation theory will certainly simplify fifth-order studies.

Quasi-degeneracy Effects.—The convergence properties of the non-degenerate formulation of the many-body perturbation theory deteriorate when quasi-degeneracy is present in the reference spectrum. In view of its simplicity, however, there is considerable interest in exploring the range of applicability of the non-degenerate formalism.

The low-lying $2p$ state in the Be atom ground state makes this a severe test of the non-degenerate perturbation series. It is an appropriate choice of system for investigating the limitations of a non-degenerate formulation of perturbation theory to systems involving near degeneracy. Full configuration mixing calculations and third-order many-body perturbation theory studies of the ground state of the beryllium atom have been performed¹⁴⁰ within the same basis sets. For a basis set containing only functions of s symmetry, there are no near degeneracy effects and the degree of agreement between the configuration mixing and perturbative studies is good. For a basis set of functions having s , p , and d symmetry, the perturbation series based on the Hartree-Fock model zero-order hamiltonian gave only 93% of the correlation correction given by the configuration mixing calculation after forming the $[2/1]$ Padé approximant to the energy series. On the other hand, by forming the $[2/1]$ Padé approximant to the shifted perturbation series, 99.5% of the configuration mixing correlation energy was recovered.

Third-order non-degenerate many-body perturbation theory studies of the ground state of the CH^+ ion have been reported.¹⁴⁵ Calculations were made using the same basis set of Slater functions employed by Green *et al.*¹⁴⁶ in their configuration mixing calculations, which included all single- and double-excitations from a two-configuration reference function. For this system quasi-degeneracy effects become increasingly important as the nuclear separation is increased. It was again demonstrated that $[2/1]$ Padé approximants to the shifted perturbation series are useful when near degeneracy is present.

One interpretation of the significance of denominator shifts, which are used in the shifted perturbation series, is that they provide a method for summing certain higher-order diagonal scattering diagrams in the model perturbation scheme to infinite order.³² In this sense, the shifted third-order results include all third-order contributions in the model scheme plus a selection of additional diagrams summed to infinite order. The quasi-degeneracy problem can be overcome in the Be atom and the CH^+ ion for internuclear distances < 4 bohr by including certain higher-order diagrammatic terms. Alternatively the shifted perturbation scheme can be interpreted as an expansion based on an alternative zero-order hamiltonian¹⁴⁷ whose spectrum does not contain near degeneracies. We prefer this latter interpretation since it represents a more balanced treatment

¹⁴⁴ V. Kvasnička, V. Laurinc, and S. Biskupič *Mol. Phys.*, 1980, **39**, 143.

¹⁴⁵ S. Wilson, *J. Phys. B: Atom. Mol. Phys.*, 1979, **12**, 1623.

¹⁴⁶ S. Green, P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine, *Phys. Rev. A*, 1972, **5**, 1614.

¹⁴⁷ P. Claverie, S. Diner, and J. Malrieu, *Int. J. Chem.*, 1967, **1**, 751.

in that all terms are included through third-order and no partial evaluation of higher-order terms is attempted.

In order to eliminate the arbitrary use of the model and shifted perturbation series, depending on the degree of degeneracy in the corresponding reference spectra, the following zero-order hamiltonian has been considered:¹⁴⁸

$$\mathcal{H}_0 = (1 - \mu)\mathcal{H}_0^{\text{model}} + \mu\mathcal{H}_0^{\text{shifted}} \quad (102)$$

where μ is an arbitrary scalar. Prototype calculations have been performed for the Be atom in which quasi-degeneracy effects arise, and for the Ne atom in which no near degeneracy is present. For both Be and Ne, $E[3/0]$ and $E[2/1]$ were found to exhibit minima with respect to μ (although it should be noted that $E[3/0]$ and $E[2/1]$ are not bounded). For the Be atom the $[2/1]$ Padé approximant to the energy series takes its minimum value at $\mu \sim 0.9$ while for Ne $E[2/1]$ is a minimum at $\mu \sim 0.2$. For Be this minimum occurs closer to $\mu = 1$, that is the shifted, or Epstein–Nesbet series, than $\mu = 0$, the model or Møller–Plesset series. The reverse situation applies in the case of the Ne atom. The $E[2/1]$ energy values for both Be and Ne are less sensitive to the value of μ than the usual power series, $E[3/0]$.

Clearly, given a set of zero-order functions which are eigenfunctions of some zero-order operator, \mathcal{H}_0 , it is possible to develop a perturbation with respect to any operator, \hat{A} , provided that $[\mathcal{H}_0, \hat{A}] = 0$. The infinite-order perturbation expansion should of course be independent of the choice of reference hamiltonian and thus the degree of agreement between two perturbation series when truncated at some finite order gives a qualitative measure of convergence. Strictly, if two perturbation expansions agree exactly at some order this does not mean that they have converged, but only that they are converging at the same rate. The use of a combination of two operators as described above allows a set of zero-order operators and the corresponding perturbation series to be investigated.

Obviously, when severe near degeneracy is present in the reference spectrum, a full quasi-degenerate formulation of the perturbation series should be employed. However, there is considerable value in applying the much simpler non-degenerate formalism to as wide a range of problems as possible.

Comparison with Other Methods.—Most methods for performing accurate calculations of the electronic properties of molecules involve some finite or infinite expansion for the wave function and the corresponding expectation values. This is the case in, for example, the method of configuration mixing, the many-body perturbation theory, cluster expansions, coupled-pair approximation, *etc.* Each method leads to the exact wave function if all terms in the expansion are evaluated. In practice, the expansions have to be truncated and methods differ only in the manner in which this truncation is effected. However, this truncation can significantly affect the theoretical properties, and to some extent the computational properties, of a method. The mere fact that one method includes more terms than another does not mean that it is superior. Which terms one leaves out is just as important as the terms one actually evaluates. Thus in the method of configuration mixing limited to single- and double-excitation with respect to a

¹⁴⁸ S. Wilson, *Chem. Phys. Lett.*, 1979, **66**, 255.

single determinantal reference function one includes many terms, corresponding to unlinked diagrams in the perturbation analysis, which cancel with terms involving higher-order excitations.

Perturbation theory provides a clearly defined order parameter in the expansion for expectation values giving a 'least-biased' indication of the importance of various terms. To quote Bradow:¹⁰⁷

'The structure of each formalism tends to suggest that certain types of approximations are most reasonable or "natural", regardless of the actual quantitative characteristics of the physical system. The many-body literature is full of papers where people have tried to make the physics fit into their preconceived approximation schemes, instead of *vice versa*. . . perturbation theory . . . seems to be the "least biased" of all the many-body techniques.'

The relationship between the coupled-electron pair approximation (c.e.p.a.) and the many-body perturbation theory has been discussed in detail by Ahlrichs.¹⁴⁹ All of the methods denoted by c.e.p.a. (x) ($x=0, 1, 2, 3$) may be related to the summation of certain classes of diagrams in the many-body perturbation theory to infinite order. For example, c.e.p.a. (0), which is Čížek's linear approximation or Hurley's c.p.a. (0) ansatz¹⁵⁰ is equivalent to the summation of all double-excitation linked diagrams in the perturbation series. This is also denoted d.e.m.b.p.t. (double excitation many-body perturbation theory) by some workers.^{151, 152}

In the coupled pair approximation,¹⁵⁰ all diagrams which can be formed by considering products of disconnected double-excitations are summed to infinite order. Thus in fourth-order, the coupled pair approximation includes the linked double-excitation and linked quadruple-excitation diagrams shown in Figure 6 and Figure 8, respectively. The coupled pair approximation may be represented diagrammatically as follows:

$$\exp \left(\text{diagram of two disconnected double excitations} \right) = 1 + \text{diagram of one double excitation} + \frac{1}{2!} \left(\text{diagram of two disconnected double excitations} \right)^2 + \dots \quad (103)$$

The order of perturbation at which various levels of excitation first arise is illustrated in Figure 11 for three different reference functions. In Figure 11(a), the Hartree-Fock orbitals are used to form the reference function, in Figure 11(b) the bare-nucleus model is used in zero-order, while in Figure 11(c) Brueckner orbitals are used to construct the reference function.

The method of single- and double-excitation configuration mixing is not size-consistent. The method remains size-inconsistent even if a multi-configurational reference function is used. For a configuration mixing calculation, with

¹⁴⁹ R. Ahlrichs, *Comput. Phys. Comm.*, 1979, **17**, 31.

¹⁵⁰ A. C. Hurley, 'Electron Correlation in Small Molecules', Academic Press, 1976.

¹⁵¹ R. J. Bartlett and I. Shavitt, *Int. J. Quantum Chem. Symp.*, 1977, **11**, 165.

¹⁵² M. R. A. Blomberg and P. E. M. Siegbahn, *Int. J. Quantum Chem.*, 1977, **14**, 583.

respect to a single determinant, a correction to fourth-order can be made by means of Davidson's formula^{2, 153, 154}

$$(1 - C_0^2) E_D \quad (104)$$

where E_D is the double-excitation configuration mixing energy and C_0 is the coefficient of the reference function. The formula^{2, 131, 155, 156}

$$\left(\frac{1 - C_0^2}{C_0^2} \right) E_D \quad (105)$$

is correct to fifth-order.

All of the methods discussed above, and some others which we have not discussed, represent a partial evaluation of fourth-order and higher-order terms in the many-body perturbation series. This must be done with great care since often there is a large degree of cancellation between terms in a given order. For example, it has been demonstrated that the two-body and many-body components of the energy are of opposite sign and for a system such as the hydrogen fluoride molecule the latter can have a magnitude which is $\approx 25\%$ of the two-body component.¹⁵⁷ In a fourth-order calculation on water, it was found that there was a significant degree of cancellation between the fourth-order double and quadruple-excitation components.¹⁵⁶

5 Computational Aspects

General Remarks.—In this section, the computational aspects of the application of the many-body perturbation theory to molecular correlation energies are discussed.

Any molecular calculation starts with the evaluation of integrals over the basis functions. This is usually, but not necessarily, followed by a self-consistent field calculation and a transformation from integrals over atomic basis functions to integrals over molecular orbitals. Full details of these particular phases of calculation are well documented elsewhere and we do not consider them further here.

Third-order calculations are considered in the next section. This is followed by a brief discussion of the computation of higher-order terms and of the evaluation of 'bubble' diagrams which are required when molecular properties are calculated or when a reference function other than the closed-shell Hartree-Fock function is employed. The impact of the new generation of computers, which have vector processing capabilities, on many-body perturbative calculations is discussed very briefly in the final section.

Third-order Many-body Perturbative Calculations.—Starting from a list of one-electron and two-electron integrals over molecular orbitals, the evaluation of the second-order and third-order energies¹²⁻¹⁴ consists of two stages. In the first stage the integrals are sorted into various types¹² while in the second stage these integral lists are used to compute the required energy components.^{13, 14}

¹⁵³ E. R. Davidson, in 'The World of Quantum Chemistry' Proceedings of the First International Congress on Quantum Chemistry, ed. R. Daudel and B. Pullman, D. Reidel, 1974.

¹⁵⁴ S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.*, 1974, **8**, 61.

¹⁵⁵ P. E. M. Siegbahn, *Chem. Phys. Lett.*, 1978, **55**, 386.

¹⁵⁶ S. Wilson and D. M. Silver, *Theor. Chim. Acta*, 1979, **54**, 83.

¹⁵⁷ S. Wilson and D. M. Silver, *J. Chem. Phys.*, 1977, **66**, 5400.

In the integral sorting phase of the calculation, the following lists of integrals are created:

$$\begin{aligned}
 (1) & \langle IJ|v|KL\rangle \\
 (2) & \langle AB|v|CD\rangle \\
 (3) & \langle IA|v|JK\rangle \\
 (4) & \langle IA|v|BC\rangle \\
 (5) & \langle IJ|v|AB\rangle \\
 (6) & \langle IA|v|JB\rangle
 \end{aligned}
 \quad v = \frac{1}{r_{12}} \quad (106)$$

where I, J, K, \dots are used to denote occupied orbitals and A, B, C, \dots are used to denote virtual orbitals. Integral types (3) and (4) are not required when a Hartree-Fock reference function is used in calculations through third-order. It is also convenient to produce a list of integrals of the form $\langle PQ|v|PQ\rangle$ and $\langle PQ|v|QP\rangle$ which are required for the denominator shift factors and, together with the one-electron integrals, to evaluate the matrix Hartree-Fock energy.

To illustrate the calculation of the energies corresponding to the four Bradow diagrams which arise through third-order we shall consider the third-order 'hole-particle' diagram in some detail.¹⁴ The various spin types which can arise are shown in Figure 12. The first step is to process the integrals of the type $\langle IJ|v|AB\rangle$. For an atom or molecule which is described by N doubly-occupied orbitals, N secondary lists are created. The I th of these secondary lists contains the integrals $\langle IJ|v|AB\rangle$ for all J and $A \geq B$, in order. The algorithm is 'integral driven.' Integrals of the type $\langle IC|v|AK\rangle$ are read into high-speed core, for all $A \geq C$ and a given $I \geq K$. Next the integrals $\langle IJ|v|AB\rangle$ and $\langle JK|v|BC\rangle$ are read into core from the I th and K th secondary lists, respectively. All integrals depending on a given I, J , and K are in core simultaneously. The integrals of the form $\langle IJ|v|AB\rangle$ and $\langle JK|v|BC\rangle$ are read for all values of J in turn until the I th and K th secondary lists have been read through completely. A new set of integrals $\langle IC|v|AK\rangle$ is then processed. For a given set of integrals depending on I, J , and K the following spin-free intermediates are formed:

$$F_{IJKAC}^1 = \sum_B \frac{(\langle IJ|v|AB\rangle - \langle IJ|v|BA\rangle)(\langle JK|v|BC\rangle - \langle JK|v|CB\rangle)}{\mathcal{D}_{IJAB}\mathcal{D}_{JKBC}} \quad (107)$$

$$F_{IJKAC}^2 = \sum_B \frac{(\langle IJ|v|AB\rangle - \langle IJ|v|BA\rangle)\langle JK|v|BC\rangle}{\mathcal{D}_{IJAB}\mathcal{D}_{JKBC}} \quad (108)$$

$$F_{IJKAC}^3 = \sum_B \frac{\langle IJ|v|AB\rangle\langle JK|v|BC\rangle}{\mathcal{D}_{IJAB}\mathcal{D}_{JKBC}} \quad (109)$$

$$F_{IJKAC}^4 = \sum_B \frac{\langle IJ|v|AB\rangle(\langle JK|v|BC\rangle - \langle JK|v|CB\rangle)}{\mathcal{D}_{IJAB}\mathcal{D}_{JKBC}} \quad (110)$$

$$F_{IJKAC}^5 = \sum_B \frac{\langle IJ|v|BA\rangle\langle JK|v|CB\rangle}{\mathcal{D}_{IJAB}\mathcal{D}_{JKBC}} \quad (111)$$

The two remaining particle states can then be summed over to give

$$g_{IJK}^{(1)} = \sum_{AC} F_{IJKAC}^{(1)} (\langle IC|v|AK\rangle - \langle IC|v|KA\rangle) \quad (112)$$

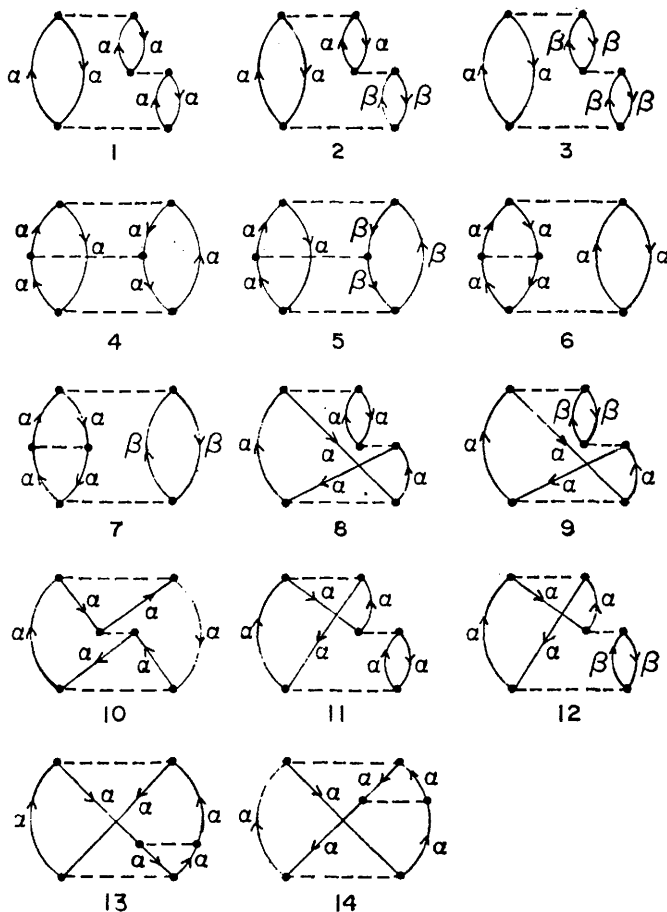


Figure 12 Spin types which arise for the third-order ring diagram

$$g_{IJ}^{(2)}K = \sum_{AC} \{F_{IJKAC}^{(3)} (\langle IC | v | AK \rangle - \langle IC | v | KA \rangle) + F_{IJKAC}^{(3)} \langle IC | v | KA \rangle\} \quad (113)$$

$$g_{IJ}^{(3)}K = \sum_{AC} F_{IJKAC}^{(3)} \langle IC | v | AK \rangle \quad (114)$$

$$g_{IJ}^{(4)}K = \sum_{AC} F_{IJKAC}^{(4)} \langle IC | v | AK \rangle \quad (115)$$

Finally, the third-order 'hole-particle' energy is given by

$$E_s(\text{hp}) = - \sum_{IJK} (g_{IJK}^{(1)} + g_{IJK}^{(2)} + g_{IJK}^{(3)} + g_{IJK}^{(4)}) \quad (116)$$

Similar algorithms have been devised to evaluate the other third-order and the second-order energy components.

Higher-order Terms.—Diagrammatic perturbation theory provides a tractable scheme for calculating the dominant components of the correlation energy which

may be associated with triple-excitations and quadruple-excitations. As an example we consider the evaluation of the quadruple-excitation fourth-order linked diagram energy component.

When the matrix Hartree-Fock operator is used as a reference hamiltonian, that is the scheme of Møller and Plesset, the evaluation of the quadruple-excitation energy component is particularly easy. Only one type of integral is required, namely the $\langle IJ|v|AB\rangle$ integrals. For a system which is described by N doubly occupied orbitals, N secondary lists are created in the manner described in the previous part of this section for the third-order hole-particle energy. The computation of the correlation energy corresponding to the diagrams shown in Figure 8 requires that certain blocks of integrals be in computer core storage simultaneously. This is achieved by two file handling schemes; one for diagram A_Q and the sum of diagrams E_Q and G_Q , and one for the sum of diagrams B_Q and C_Q , and D_Q and E_Q . In our method, diagram A_Q and the sum of E_Q and G_Q are evaluated by employing the same file handling scheme. Blocks (IJ) and (JK) are placed in core storage simultaneously. This is done by reading simultaneously through the I th and K th secondary lists for all values of J . The I th and K th secondary lists are read through completely for each value of I and K . When computing the energy component corresponding to the sum of diagrams B_Q and C_Q , we require blocks (IJ) and (KL) in core storage at the same time. This is achieved by reading the block (IJ) from the primary list of integrals, rewinding and reading all (KL) less than (IJ) . The next value of (IJ) can then be treated, the file rewound and the whole process repeated.

Spin orthogonalities considerably simplify the computations. For example, in the evaluation of diagram A_Q six spin-free intermediates can be defined. Three of these take the form

$$f_{IKBD}^{(1)} = \sum_A \frac{(\langle IJ|v|AB\rangle - \langle IJ|v|BA\rangle)(\langle KJ|v|AD\rangle - \langle KJ|v|DA\rangle) + \langle IJ|v|BA\rangle\langle KJ|v|DA\rangle}{\mathcal{D}_{IJAB}} \quad (117)$$

$$f_{IKBD}^{(2)} = - \sum_A \frac{(\langle IJ|v|AB\rangle - \langle IJ|v|BA\rangle)\langle KJ|v|DA\rangle + \langle IJ|v|BA\rangle(\langle KJ|v|AD\rangle - \langle KJ|v|DA\rangle)}{\mathcal{D}_{IJAB}} \quad (118)$$

$$f_{IKBD}^{(3)} = \sum_A \frac{\langle IJ|v|AB\rangle\langle KJ|v|AD\rangle}{\mathcal{D}_{IJAB}} \quad (119)$$

while the remaining three merely include an extra denominator factor [see equation (95)]. The energy corresponding to diagram A_Q is then given by

$$E_A(A_Q) = \sum_{IK} \sum_{BD} \{f_{IKBD}^{(1)}g_{IKBD}^{(1)} + f_{IKBD}^{(2)}g_{IKBD}^{(2)} + f_{IKBD}^{(3)}g_{IKBD}^{(3)}\} \quad (120)$$

We note that iterative schemes have been devised¹⁵¹ to evaluate higher-order diagrams involving double-excitations. These schemes can easily be generalized to handle triple-excitations and quadruple-excitations.

Bubble Diagrams.—The bubble diagrams which are shown in Figures 13 and 14 are required when the reference function for a closed-shell system is not defined by the matrix Hartree-Fock model, when a restricted Hartree-Fock reference

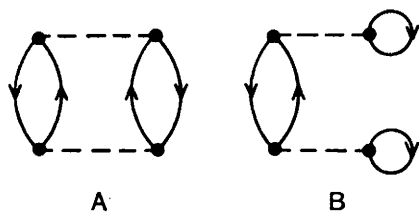


Figure 13 *Second-order diagrams which arise when electron-electron interactions are completely neglected*

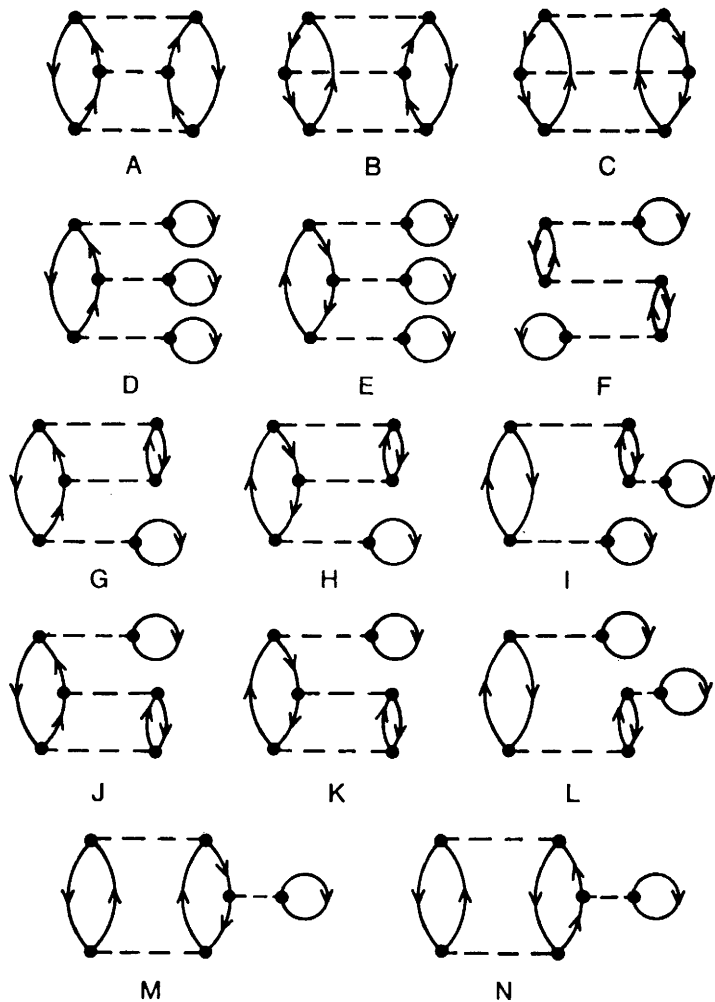


Figure 14 *Third-order diagrams which arise when electron-electron interactions are completely neglected*

function is used for open-shell systems, or when molecular properties are to be evaluated. General programs have been written which allow any arbitrary one-electron operator matrix elements to be used in the evaluation of the bubble diagrams.¹⁵⁸ The expressions corresponding to each of the diagrams in Figure 13 are as follows

$$E_2(A) = \frac{1}{4} \sum_{ij} \sum_{ab} \frac{\mathcal{J}_{ijab} \mathcal{J}_{ijab}}{\mathcal{D}_{ijab}} \quad (121)$$

$$E_2(B) = \sum_i \sum_a \frac{\Lambda_{ia} \Lambda_{ai}}{\mathcal{D}_{ia}} \quad (122)$$

where Λ is the 'bubble' matrix.

The expressions corresponding to the diagrams shown in Figure 14 are as follows

$$E_3(A) = \frac{1}{8} \sum_{ij} \sum_{abcd} (\mathcal{J}_{ijab} \mathcal{J}_{cdab} \mathcal{J}_{cdij}) / (\mathcal{D}_{ijab} \mathcal{D}_{ijcd}) \quad (123)$$

$$E_3(B) = - \sum_{ijk} \sum_{abc} (\mathcal{J}_{ijab} \mathcal{J}_{katic} \mathcal{J}_{bcjk}) / (\mathcal{D}_{ijab} \mathcal{D}_{jkbc}) \quad (124)$$

$$E_3(C) = \frac{1}{8} \sum_{ijkl} \sum_{ab} (\mathcal{J}_{ijab} \mathcal{J}_{klij} \mathcal{J}_{abkl}) / (\mathcal{D}_{ijab} \mathcal{D}_{klab}) \quad (125)$$

$$E_3(D) = \sum_i \sum_{ab} (\Lambda_{ia} \Lambda_{ab} \Lambda_{bi}) / (\mathcal{D}_{ia} \mathcal{D}_{ib}) \quad (126)$$

$$E_3(E) = - \sum_{ij} \sum_a (\Lambda_{ai} \Lambda_{ij} \Lambda_{ja}) / (\mathcal{D}_{ia} \mathcal{D}_{ja}) \quad (127)$$

$$E_3(F) = \sum_{ij} \sum_{abc} (\Lambda_{ia} \mathcal{J}_{ibaj} \Lambda_{bj}) / (\mathcal{D}_{ia} \mathcal{D}_{jb}) \quad (128)$$

$$E_3(G) = \sum_{ij} \sum_{abc} (\mathcal{J}_{ijab} \mathcal{J}_{abcf} \Lambda_{fc}) / (\mathcal{D}_{ijab} \mathcal{D}_{ic}) \quad (129)$$

$$E_3(H) = - \sum_{ijk} \sum_{ab} (\mathcal{J}_{ijab} \mathcal{J}_{kbij} \Lambda_{ka}) / (\mathcal{D}_{ijab} \mathcal{D}_{ka}) \quad (130)$$

$$E_3(I) = \sum_{ij} \sum_{ab} (\mathcal{J}_{ijab} \Lambda_{jb} \Lambda_{ia}) / (\mathcal{D}_{ijab} \mathcal{D}_{ia}) \quad (131)$$

$$E_3(M) = -\frac{1}{2} \sum_{ijk} \sum_{ab} (\mathcal{J}_{ijab} \Lambda_{jk} \mathcal{J}_{ikab}) / (\mathcal{D}_{ijab} \mathcal{D}_{ikab}) \quad (132)$$

$$E_3(N) = \frac{1}{2} \sum_{ij} \sum_{abc} (\mathcal{J}_{ijab} \Lambda_{bc} \mathcal{J}_{acij}) / (\mathcal{D}_{ijab} \mathcal{D}_{iac}) \quad (133)$$

The energy associated with diagram G is the complex conjugate of that associated with diagram J. Diagrams H and K, I and L are similarly related.

Vector Processing Computers.—We conclude this section by considering briefly the impact which vector-processing computers are likely to have on many-body perturbative calculations in the near future. As noted in the previous subsection, use of the CRAY 1 has already enabled the triple-excitation component of the correlation energy to be evaluated for a molecule using a fairly large basis set.¹³⁸

The algorithms devised to perform many-body perturbation calculations are well suited to vector processing computers such as the CRAY 1.^{141, 159} The scalar

¹⁵⁸ S. Wilson and D. M. Silver, unpublished work.

¹⁵⁹ R. W. Hockney, *Contemp. Phys.* 1979, **20**, 149; M. F. Guest and S. Wilson, 'Proceedings of the American Chemical Society Symposium on Supercomputers in Chemistry', Las Vegas, 1980.

operations on this machine are about twice as fast as those of the CDC 7600 or the IBM 370/195 whereas the measured time on the CRAY 1 for matrix multiplication, using the vector order repertoire is twenty times faster than the best hand-coded routines on the CDC 7600 or IBM 370/195.

The innermost loop in the program written to evaluate the triple-excitation energy component described in the previous subsection has the form

```
DO 1 ID=1, N
  DD(ID)=D1(ID)*D2(ID)
  DE(ID)=D1(ID)*E2(ID)
  ED(ID)=E1(ID)*D2(ID)
  EE(ID)=E1(ID)*E2(ID)
1 CONTINUE
```

where D1 and D2 contain direct integrals and E1 and E2 exchange integrals. We performed a timing test for this loop and the results are shown in Table 2.

Table 2 CPU times on the CRAY 1 and the IBM 360/195 computer required to execute the inner loop in the evaluation of the triple-excitation energy component

<i>N</i> ^a	<i>Time</i> ^b	
	CRAY 1 ^c	IBM 360/195 ^a
16	3.6	41.8
32	5.2	82.9
48	6.8	124.4
64	8.4	165.6

^a DO-loop range defined in text. ^b CPU time in microseconds. ^c Using vector order repertoire.

^d FORTRAN H extended plus compiler with OPT=2.

The efficiency of algorithms based on diagrammatic perturbation theory together with the capabilities of the new generation of vector-processing computers will allow increasingly large basis sets to be employed over the next few years, thus reducing one of the major sources of error in present-day molecular calculations, the basis set truncation error.¹⁶⁹

6 Some Applications

General Remarks.—In this section we attempt to give a brief overview of the accuracy of electron correlation calculations which are possible at present using many-body perturbation theory. In the first part we describe some new calculations on the lithium dimer and some previously reported work⁹² on the nitrogen molecule. In the second part we review the application of many-body perturbation theory to potential energy curves. In part three, the importance of triple-excitations and quadruple-excitations is discussed in the light of recent calculations. The calculation of molecular properties is discussed in the final part of this section.

Application to Li_2 , N_2 .—The results of calculations through third-order are shown in Table 3 and Table 4 for the lithium dimer and the nitrogen molecule, respectively. These calculations were performed by using the universal basis set containing functions with s , p , and d symmetry described in Section 3. For the lithium dimer the calculations were performed at an internuclear distance of 5.0507 bohr, the experimental equilibrium value, whereas for the nitrogen molecule the calculations were performed for a nuclear separation of 2.0 bohr. The experimental equilibrium nuclear separation in the nitrogen molecule is 2.068 bohr. The second-order and third-order energy components are given for both the model perturbation series and the perturbation series using shifted denominators. In addition to the simple perturbation results, [2/1] Padé approximants and variational upper bounds are presented.

The model perturbation series is observed to converge more rapidly than the shifted expansion, if we use the ratio of the third-order energy to the second-order energy as a measure of the rate of convergence. Note that for the total energies shown in Tables 3 and 4, the Padé approximants resulting from the two perturbation series are in closer agreement than the simple third-order energies. The difference between $E[3/0]$ and $E[2/1]$ is smaller for the model scheme than the shifted expansion. The $E[2/1]$ values derived from the model scheme are thus of most interest although the optimized upper bound is also useful. The empirical correlation energy of the lithium dimer is estimated to be -0.126 hartree. For the model perturbation series the formation of [2/1] Padé approximants leads to

Table 3 *Components of the calculated correlation energy for the lithium dimer obtained using third-order perturbation theory and an s,p,d universal basis set^a*

	<i>Model series</i>	<i>Shifted series</i>
E_{scf}	-14.871 23	-14.871 23
$E[2/0]$	-14.969 20	-14.993 76
$E[3/0]$	-14.982 19	-14.983 74
$E[2/1]$	-14.984 17	-14.984 49
$E_{\text{var}}(\lambda=1)$	-14.978 31	-14.968 99
$E_{\text{var}}(\lambda_{\text{opt}})$	-14.979 20	-14.972 76
λ_{opt}	1.102 08	0.828 63

^a In hartrees.

Table 4 *Components of the calculated correlation energy for the nitrogen molecule obtained using third-order perturbation theory and an s,p,d universal basis set^a*

	<i>Model series</i>	<i>Shifted series</i>
E_{scf}	-108.992 10	-108.992 10
$E[2/0]$	-109.439 08	-109.523 85
$E[3/0]$	-109.436 76	-109.401 38
$E[2/0]$	-109.436 77	-109.424 31
$E_{\text{var}}(\lambda=1)$	-109.392 51	-109.335 28
$E_{\text{var}}(\lambda_{\text{opt}})$	-109.396 54	-109.380 01
λ_{opt}	0.904 8	0.729 5

^a In hartrees.

a calculated correlation energy of -0.1129 hartree which corresponds to 89.6% of the empirical estimate. Formation of an upper bound leads to a correlation energy of -0.1080 hartree which is 85.7% of the estimated total correlation energy.

For the nitrogen molecule calculations were performed for nuclear separations of 1.75, 2.00, 2.25, and 2.50 bohr and these values interpolated to obtain a correlation energy at the equilibrium nuclear geometry. The empirical correlation energy for the nitrogen molecule is -0.538 hartree. The calculated correlation energy obtained by interpolation is -0.4501 hartree which represents 83.7% of the estimate.

Both of the calculations described above recover a greater percentage of the correlation energy than previous studies. There are two deficiencies in the above calculations. The first, and probably the major effect, is that resulting from truncation of the basis set used in invoking the algebraic approximation. The concept of a universal even-tempered basis set should go a long way towards developing the large basis sets which are ultimately going to be required in order to achieve chemical accuracy (one millihartree). The basis sets used in the calculations described above do not include functions with ϕ symmetry which will be required for an accurate description of angular correlation effects. The second deficiency results from the truncation of the perturbation series at third-order. Results of calculations for the water molecule will be discussed more fully in the fourth part of this section. We feel that it is always important to evaluate all terms, through whatever order the perturbation series is taken.

Potential Energy Curves.—Potential energy curves have been calculated by many-body perturbation theory for a number of diatomic molecules, including FH,¹⁶⁰ CO,^{92,161} CS,¹⁶² N₂,^{92,163} BF,⁹² F₂,¹⁶³ Be₂,¹⁶⁴ Mg₂,¹⁶⁵ We take the results for the FH molecule as representative.

The potential energy curves for FH are shown in Figure 15. Curves (d) and (e) in this Figure were determined by third-order many-body perturbation calculations. Full details of the calculations can be found elsewhere.¹⁶⁰ Curve (a) is the potential energy curve obtained by the self-consistent-field approximation. Curves (b) and (c) were determined by Dunning¹⁶⁶ using the generalized valence bond method and by Meyer and Rosmus¹⁶⁷ using the coupled electron pair method, respectively. Curve (d) corresponds to the upper bound determined from third-order perturbation calculations using the model perturbation series and curve (e) to the [2/1] Padé approximant constructed from this series. Morse curves derived from experimental data are labelled (f) and (g). Curve (f) includes a correction for relativistic effects and represents an estimate of the nonrelativistic potential energy curve.

¹⁶⁰ S. Wilson, *Mol. Phys.*, 1978, 35, 1.

¹⁶¹ S. Wilson, *Int. J. Quantum Chem.*, 1977, 12, 604.

¹⁶² S. Wilson, *J. Chem. Phys.*, 1977, 67, 4491.

¹⁶³ M. Urban and V. Kello, *Mol. Phys.*, 1979, 38, 1621.

¹⁶⁴ R. J. Bartlett and G. D. Purvis, *Int. J. Quantum Chem. Symp.*, 1978, 14, 561; M. R. A. Blomberg and P. E. M. Siegbahn, *ibid.*, p. 583; M. A. Robb and S. Wilson, *Mol. Phys.*, 1980, 40, 1333.

¹⁶⁵ R. J. Bartlett and G. D. Purvis, *J. Chem. Phys.*, 1978, 68, 2114.

¹⁶⁶ T. H. Dunning Jr., *J. Chem. Phys.*, 1976, 65, 3854.

¹⁶⁷ W. Meyer and P. Rosmus, *J. Chem. Phys.*, 1975, 63, 2356.

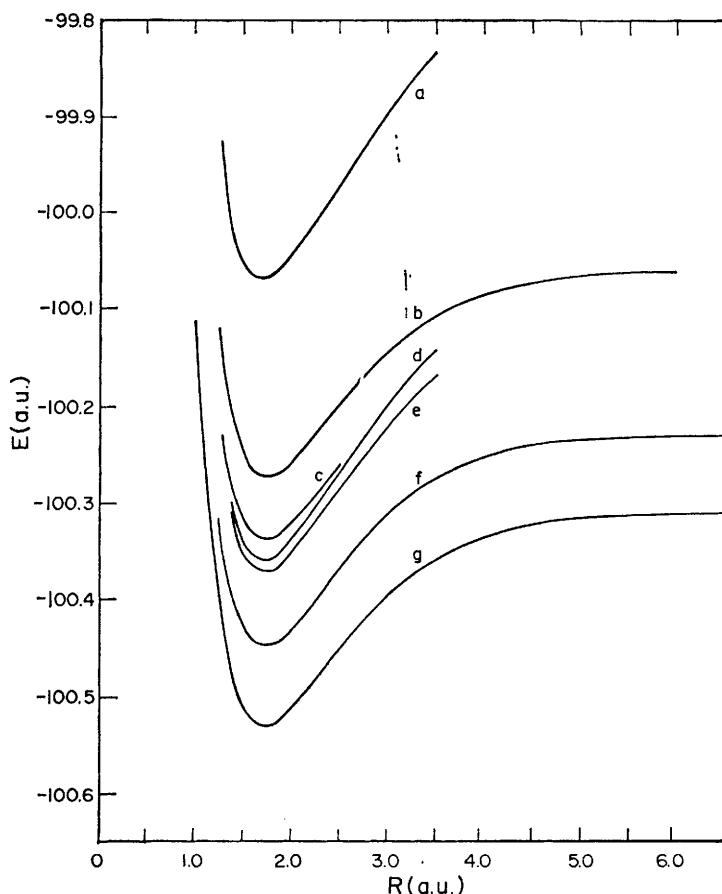


Figure 15 Potential energy curve for the hydrogen fluoride molecule

The equilibrium nuclear distance determined from the self-consistent-field curve is 0.897 \AA which differs by 2.2% from the experimentally determined value of 0.917 \AA . Curve (e) yields an equilibrium distance of 0.908 \AA , which differs by 1.0% from the experimentally determined value. The fundamental frequencies of vibration derived from curves (a), (e), and (g) are 4471 , 4261 , and 4137 cm^{-1} , respectively.

Triple-excitations and Quadruple-excitations.—Only double excitations contribute to the correlation energy and other properties through third-order; triple-, quadruple and higher-order excitations are usually neglected. Triple- and quadruple-excitations first arise in the fourth-order of the perturbation series.

To illustrate the importance of triple and quadruple excitations we present in Table 5 a full fourth-order calculation for the water molecule.^{138, 139, 156} This calculation corresponds to the equilibrium nuclear geometry and the basis set of

Table 5 Contribution of triple-excitations and quadruple-excitations to the correlation energy of the water molecule at its equilibrium nuclear geometry

Diagram	Triple ^a excitation energy	Quadruple excitation energy
A	-2.29	-7.14
B	-1.33	-1.02
C	-1.35	
D	-2.39	+3.51
E	-9.42	
F	-7.11	+7.86
G	-5.94	
H	-7.77	
I(L)	+2.36	
J(K)	+9.73	
M(N)	+1.53	
O(P)	+1.15	
Total linked diagram energy	-7.86	+3.21
Unlinked diagram energy	—	-17.11
$E[2/1]^b$	-0.285 1	
E_{4S}^b	-0.002 0	
E_{4D}^b	-0.004 3	

• In millihartrees. ^b In hartrees.

39 Slater functions first presented by Rosenberg and Shavitt.¹⁶⁸ The quadruple-excitation component can be divided into a part which corresponds to unlinked diagrams and a part which corresponds to linked diagrams. The unlinked diagram is only of interest since it represents the largest contribution to the size-consistency error in the widely used method of configuration interaction limited to single and double excitations with respect to a single-determinantal reference function.

It can be seen that the linked triple excitation energy is in fact quite large and certainly chemically significant. There is clearly a danger in any technique which attempts to make a partial evaluation of higher order terms in the perturbation series.^{181, 156}

Molecular Properties.—Kelly⁵ showed that the many-body perturbation theory provides a powerful method for the calculation of atomic polarizabilities. Typical diagrams which arise in such calculations are shown in Figure 16. Itagaki and Saika^{126, 127} have extended Kelly's work to molecules. The present author¹²⁰ has demonstrated how the use of a scaling parameter can lead to improved results in such calculations. Itagaki and Saika have also very recently reported applications to nuclear spin-spin coupling constants.¹⁶⁹

Many-body perturbation theory can also form the basis of a useful technique for the calculation of photoionization effects in atom and molecules. Kelly has recently reviewed this area of research.¹⁷⁰

¹⁶⁸ B. J. Rosenberg and I. Shavitt, *J. Chem. Phys.*, 1975, **63**, 2163.

¹⁶⁹ T. Itagaki and A. Saika, *J. Chem. Phys.*, 1979, **70**, 2378.

¹⁷⁰ H. P. Kelly, *Comput. Phys. Comm.*, 1979, **17**, 99.

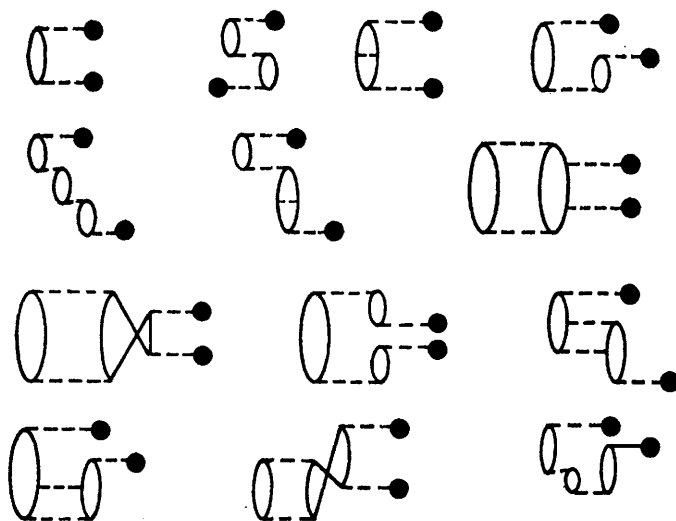


Figure 16 Diagrams which arise in the calculation of polarizabilities. The heavy dot represents a dipole moment matrix element

7 Concluding Remarks

General Remarks.—In this final section, some other aspects of the many-body perturbation theory of molecules are briefly reviewed. The final comments address the general properties which we believe methods for treating electron correlation in molecules must possess.

Some Other Aspects.—In 1972, Coulson (quoted in ref. 6) suggested that diagrammatic techniques would become increasingly important in theoretical chemistry. The impact of diagram methods is perhaps only just being fully realized. In this section very recent work and possible directions for future research are discussed. In particular an extension of the work described in the second part of section 4 on invariants is described, the possibility of employing group-theoretical developments in many-body perturbation theory is indicated, recent work on electron-molecule scattering is mentioned, and the calculation of energy derivatives is briefly discussed.

Even-order Invariants for Rayleigh-Schrödinger Perturbation Theory. Full fourth-order correlation energy calculations are now possible and it is, therefore, important to have fourth-order forms which share the invariance properties of the [2/1] Padé approximants in third-order. The expression

$$E[2/1] + \left(\frac{E[2/1]}{E_2} \right)^3 \left(E_4 - \frac{E_3^2}{E_2} \right) \quad (134)$$

where

$$E[2/1] = E_2 / (1 - E_3/E_2) \quad (135)$$

has recently, been shown to be useful in this respect.¹⁷¹

¹⁷¹ S. Wilson, *Int. J. Quantum Chem.*, in press.

Graphical Methods of Spin Algebras. In most problems of chemical interest, the molecular hamiltonian can be taken to be spin-free and can be written^{172,173} in terms of the generators of the unitary group, $U(n)$, where n is the number of basis functions

$$\mathcal{H} = \sum_{ab} \langle a|z|b \rangle + \frac{1}{2} \sum_{abcd} \langle ab|v|cd \rangle (\mathcal{E}_{ac}\mathcal{E}_{bd} - \zeta_{bc}\mathcal{E}_{ad}) \quad (136)$$

in which

$$\mathcal{E}_{ab} = \sum_{\sigma} a_{a\sigma}^{\dagger} a_{b\sigma} \quad (137)$$

and a^{\dagger} and a are the usual creation and annihilation operators. A spin-adapted perturbation expansion can be obtained by defining

$$\mathcal{H}_0 = \sum_a \langle a|f|a \rangle \mathcal{E}_{aa} \quad (138)$$

and

$$\mathcal{H}_1 = \frac{1}{2} \sum_{abcd} \langle ab|v|cd \rangle (\mathcal{E}_{ac}\mathcal{E}_{bd} - \delta_{bc}\mathcal{E}_{ad}) + \sum_{ab} \{ \langle a|z|b \rangle \mathcal{E}_{ab} - \delta_{ab} \langle a|f|b \rangle \mathcal{E}_{ab} \} \quad (139)$$

The matrix elements of the generators, \mathcal{E}_{ab} , can be evaluated using the graphical methods of spin algebra.¹⁷⁴⁻¹⁷⁶ The particle-hole formalism introduced by Flores and Moshinsky¹⁷⁷ and recently discussed by Paldus and Boyle¹⁷⁸ is most suitable for such developments.

Electron-Molecule Scattering. Kaldor and co-workers¹⁷⁹ have recently shown that diagrammatic perturbation theory can be used to expand the optical potential in electron-molecule scattering calculations. The second-order diagrams, including those resulting from electron exchange are shown in Figure 17.

Padé Approximants to Energy Derivatives. The evaluation of derivatives of the energy, with respect to the nuclear geometry, forms the basis of an efficient approach to the calculation of potential energy curves and surfaces. It is easily shown that

$$\frac{d^m}{d\rho^m} \tilde{E}_n(\rho) = \frac{1}{\mu^{n-1}} \sum_{k=2}^n \binom{n-2}{k-2} (\mu-1)^{n-k} \frac{d^m}{d\rho^m} E_k(\rho) \quad (140)$$

where

$$\rho = \frac{r-r_e}{r_e} \quad (141)$$

¹⁷² J. Paldus, *Theor. Chem., Advances and Perspectives*, 1976, **2**, 131.

¹⁷³ I. Shavitt, *Int. J. Quantum Chem., Symp.*, 1978, **12**, 5; and in 'Proceedings of Daresbury Study Weekend', November 1979, ed. M. F. Guest and S. Wilson, Science Research Council, 1980.

¹⁷⁴ A. P. Yutsis, I. Levinson, and V. Vanagas, 'Mathematical Approaches of the Theory of Angular Momentum' Israel Program for Scientific Translation, 1962.

¹⁷⁵ E. El Baz and B. Castel, 'Graphical Methods of Spin Algebras', Dekker, New York, 1972.

¹⁷⁶ S. Wilson, in 'Proceedings of Daresbury Study Weekend', November 1979, ed. M. F. Guest and S. Wilson, Science Research Council, 1980.

¹⁷⁷ J. Flores and M. Moshinsky, *Nucl. Phys.*, 1967, **A93**, 81.

¹⁷⁸ J. Paldus and M. Boyle, *Physica Scripta*, 1980, **21**, 295; M. Boyle, Dissertation, University of Waterloo, 1979; J. Paldus, in 'Proceedings of Daresbury Study Weekend', November 1979, ed. M. F. Guest and S. Wilson, Science Research Council, 1980.

¹⁷⁹ A. Klonover and U. Kaldor, *J. Phys. B: Atom. Mol. Phys.*, 1978, **11**, 1623; *ibid.*, 1979, **12**, 323.

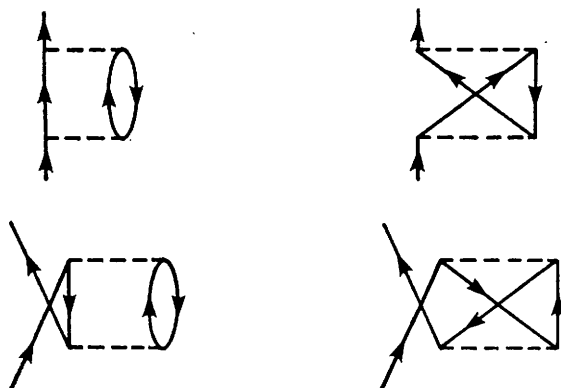


Figure 17 Second-order diagrams for electron molecule scattering

E_k is the k th order energy corresponding to the zero-order hamiltonian \mathcal{H}_0 and \tilde{E}_k is the k th order energy corresponding to $\mu\mathcal{H}_0$. It therefore follows that the $[N+1/N]$ Padé approximants to the energy derivatives share the invariance properties of the $[N+1/N]$ Padé approximants to the energy itself.

Final Comments.—Many-body perturbation theory has several theoretical properties that make its use in molecular studies attractive. If a system is composed of non-interacting subsystems, then this fact should be evident at any level of the theory. It is possible to formulate any quantum mechanical problem in such a way that, if the whole system is separated into subsystems, all quantities appearing in this formalism are additive. There is a close connection between this question of additivity of properties and linked diagram expansions and Lie algebraic formulations of quantum mechanics. Many-body perturbation theory provides a formulation of the correlation problem which satisfies these requirements. The energy of any system is always written as a sum of the energies of its component parts. The energy is written in terms of single-particle state functions rather than N -electron functions. These theoretical properties lead to tractable computational schemes for treating correlation effects with little more effort than a conventional self-consistent field calculation.¹⁸⁰

Coulson¹⁸¹ thought that it would take 15 years for the impact of diagrammatic techniques to be fully realized in theoretical chemistry. It is therefore not surprising that the first half of this period has been devoted mainly to the development of new methods and algorithms. Although this development will undoubtedly continue, it is clear that, armed with these new techniques, theoretical chemists will be able to attack problems with an accuracy which was not previously attainable. For example, it will be possible to calculate rotation constants for small molecules more precisely. Although the accuracy of calculated rotation

¹⁸⁰ M. F. Guest and S. Wilson, 'Proceedings of the American Chemical Society Symposium on Supercomputers in Chemistry', Las Vegas, 1980.

¹⁸¹ C. A. Coulson, 1973, Progress Report, Department of Theoretical Chemistry, Oxford, 1972—73.

constants will still not match that of microwave experiments, calculations are of great value when experiments are difficult or impossible. In the past few years, theoretical studies have been of great value in the detection of certain interstellar radicals and ions¹⁸² that are very difficult to study in terrestrial experiments.

¹⁸² S. Wilson, *Chem. Rev.*, 1980, **80**, 263.